UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF CHEMICAL SAFETY
AND POLLUTION PREVENTION

MEMORANDUM

Date: May 13, 2014

Subject: Risk Assessment for the Proposed Registration of the New Use of Cuprous Oxide, Zinc and Silver as a Thermostatic Antifouling Powered Coating for Use on Boat and Ship Hulls and Marine Structures

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Decision No.: 462764	Registration Number (s): 89101-R
Regulatory Action: A490 New Use; Outdoor; Nonfood	Risk Assess Type: Multiple active ingredients
CAS No(s): 1317-39-1; 7440-66-6; 7440-22-4	MRID No(s).: multiple, see References

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Executive Summary

The Antimicrobials Division (AD) of the Office of Pesticide Programs (OPP) is charged with estimating the risk to human health and the environment from the exposure to pesticides. Reintjes Marine Surface Technologies, LLC has requested registration of a new thermoplastic antifouling powder coating for use on boat and ship hulls and marine structures (Tefcite). The Regulatory Management Branch I (RMBI) of AD has requested that the Risk Assessment and Science Support Branch (RASSB) conduct dietary, residential, occupational, and environmental fate assessments, as needed, in order to estimate the risk to human health and the environment that will result from this proposed use of cuprous oxide, and metallic silver, and zinc.

RASSB has evaluated the toxicity and fate databases for copper, silver, and zinc and has conducted human health and ecological risk assessments which are provided in this document. The active ingredients in the antifoulant are conventional inorganic complexes of the metal for which conventional fate data (e.g., hydrolysis, biotic degradation) is not required. Information on particle size distribution of the product and leaching rates of the metals from the paint were provided by the registrant. Ecological effects data used in the assessment are based primarily on information from Office of Water (OW) water quality criteria documents and sediment benchmark documents. Recently AD has added freshwater marina scenarios to assessment of antifoulant paints. In the case of metals this means the agency needs to consider the impact of water chemistry on the effect level for aquatic organisms but that such risks have also not been considered for most other antifoulant paints. Except for copper, freshwater criteria are based on hardness-dependent relationships which can be parameterized with relative ease to reflect national ranges. However, the current ambient water quality criterion method for developing acute copper criteria is based on a biotic ligand model and requires inputs for a number of water chemistry factors. Except for temperature, pH, and DOC, such factors are not included in the exposure model used for the ecological assessment, nor have they been parameterized for conducting a national assessment at this time. Therefore for assessing risks to the freshwater environment the previous copper hardness-dependent relationship was used to account for effects of water chemistry on toxicity. Impacts of key modeling assumptions and uncertainties for the ecological risks such as the biotic ligand method, maximum versus steady-state leach rates were considered in risk conclusions.

Based on this assessment, RASSB has determined that there are no potential human health risk estimates of concern for the proposed use of cuprous oxide, and metallic silver and zinc in Tefcite provided applicators wear respirators with a protection factor (PF) of at least 25 as required by the label. RASSB has determined that there are potential ecological risk estimates of concern in marinas primarily due to copper leaching from Tefcite, but they are expected to be within similar levels of concern for other registered antifoulant paints with these metals.

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1 Introduction

Tefcite is proposed for use as a durable antifoulant coating for use in both freshwater and marine environments. The active ingredients in Tefcite are cuprous oxide, and metallic zinc, and silver. These ingredients are part of a powder coating that is applied to boats and stationary structures using a thermoplastic spray gun that melts inert components of the material product as it is being sprayed to form a film.

1.1 Product Chemistry

Tefcite is formulated as a powder and contains 56% cuprous oxide (Cu_2O), 0.054% zinc (Zn^0), and 0.018% silver (Ag^0). The copper in Tefcite is in the +1 oxidative state, and silver and zinc are in the 0 oxidative state.

1.2 Particle Size

Particle size data indicate that Tefcite powder has a particle size distribution of 0.25 to 126 microns (MRID 48858402). Approximately 20.7 % of the product contains particle sizes 0.25-20 microns with a peak of 13 microns and the remaining (79.3%) has particle sizes ranging from 20 to 126 microns with a peak of 63 microns.

2 Human Health Risk Assessment

2.1 Hazard Characterization and Dose-Response Assessment

2.1.1 Silver

The Agency's hazard database for silver and silver compounds is limited. A Reregistration Eligibility Decision (RED) document for Silver was issued in 1993.

In 2009, The Agency issued a Registration Review Preliminary Work Plan (PWP) for Silver and Silver Compounds. The Registration Review PWP concluded that the existing toxicological databases for silver and silver compounds were not sufficient for characterizing hazard and risk from exposure to these chemicals and identified toxicity data gaps including 90-day inhalation toxicity, reproductive toxicity, chronic toxicity, and neurotoxicity screening battery.

Toxicity studies included in the RED and Registration Review PWP were located primarily in the open literature, including subchronic toxicity, developmental toxicity and mutagenicity studies.

In a National Toxicology Program (NTP) developmental study conducted for EPA's Office of Solid Waste and Emergency Response (OSWER), Sprague-Dawley-derived (CD) rats were dosed by gavage with silver acetate in 1% aqueous methylcellulose at dose levels of 10, 30, or 100 mg/kg/day (equivalent to approximately 6.5, 19.4, or 64.6 mg silver/kg/day) or vehicle on gestational days (GD) 6 through 19. Treatment-related clinical signs noted primarily in the mid and high-dose groups and consisted of weight loss, rooting after dosing, and piloerection. No other maternal adverse effects were shown and no developmental toxicity was reported.

In a subchronic mice study and chronic studies in rats, silver nitrate, at various concentrations equivalent to 65 mg/kg/day (mice) and 63.5 and 130 mg/kg/day (rats) in drinking water for 12 days to 14 weeks (mice) and up to life time exposure, did not induce any toxicity. However, silver deposits were observed in the basement membrane of the kidneys and other organs, including liver, colon, choroid plexus, thyroid acinar, skin appendage basement membranes and surface as well as urinary bladder, at necropsy. There was an increase in the relative weight (to body) of the left ventricle in rats treated with silver nitrate in drinking water at 63.5 mg/kg/day for life-time exposure.

Silver deposits were also observed in large motor neurons and protoplasmic astrocytes as well as in the hippocampus, brain stem motor nuclei, cerebellum, globus pallidus, and spinal cord in a few studies that investigated silver lactate in rats (both adults and pups). The toxicological significance of silver deposits in nervous system needs to be examined further.

Silver metal was found to be non-mutagenic but induced deoxyribonucleic acid (DNA) strand breaks and caused reduction in molecular weight of DNA. Silver nitrate was not mutagenic when tested up to a concentration of 0.1μM by UV light in E coli WP2.

2.1.2 Zinc

There is no RED or Registration Review PWP for zinc and no quantitative toxicity assessment conducted by the Agency. A Toxicological Profile for Zinc published by the Agency for Toxic Substances and Disease Registry (ATSDR) was located in the literature. Some adverse effects associated with zinc deficiency and exposure to zinc/zinc salts acutely and/or during a long period of time are summarized in the text below.

Zinc is ubiquitous in the environment, mainly as zinc oxide (ZnO) or sphalerite (ZnS). It is an essential nutrient in the human body and necessary for the function of a large number of metalloenzymes. Adverse effects associated with zinc deficiency in humans include dermatitis, anorexia, growth retardation, poor wound healing, hypogonadism with impaired reproductive capacity, impaired immune function, and depressed mental function; increased incidence of congenital malformations in infants born to the mothers with zinc deficiency. Additionally, exposure to high level of zinc also resulted in adverse effects in humans and animals. The most commonly reported adverse effect in humans after acute inhalation of zinc oxide, as well as other zinc metals (to a lesser extent), is a condition called "metal fume fever", characterized by chest pain, cough, dyspnea, reduced lung volumes, nausea, chills, malaise, and leukocytosis. The symptoms appear fairly fast within a few hours after exposure via the inhalation route and are reversible in 1–4 days following cessation of exposure. Acute inhalation exposure to zinc oxide resulted in pulmonary changes, such as grayish areas with pulmonary congestion, various degrees of peribronchial leukocytic infiltration, and bronchial exudate, in rats and rabbits. Gastrointestinal irritation (nausea, vomiting, abdominal cramps, and diarrhea with/without blood) have also been reported in humans after acute inhalation of zinc oxide and zinc sulfate.

Longer-term exposed to lower dose zinc compounds (~0.5-2 mg Zn/kg/day) orally resulted in decreased absorption of copper from the diet. The most noticeable manifestation of the decreased copper level is anemia (decreased erythrocyte number or hematocrit).

Dermal exposure to zinc or zinc compounds generally does not result in any noticeable toxic effects. Severe skin irritation has been reported in dermal exposure to zinc chloride or other zinc salts (to a lesser extent).

2.1.3 Copper

The Agency issued a Reregistration Eligibility Decision (RED) for Coppers in 2006. A Toxicological Profile of Copper published by ATSDR was located in the literature (ATSDR, 2004).

Copper occurs naturally and is ubiquitous in food and drinking water. Copper is an essential nutrient in the human body, which plays a critical role in "a number of metalloenzymes involved in hemoglobin formation, drug/xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the cross-linking of collagen, elastin, and hair keratin, and the antioxidant defense mechanism" (ATSDR, 2004).

Current available literature and studies do not indicate any systemic toxicity associated with dietary exposures to copper. However, some genetic disorders such as Wilson's Disease, Occipital Horn Syndrome, Tyrolean Infantile Cirrhosis, Indian Childhood Cirrhosis, Idiopathic Copper Toxicosis, can disrupt the metabolism of copper in the human body. Generally, current available data and literature studies indicate that there is a greater risk from the deficiency of copper intake than from excess intake (U.S EPA, 2008). Transient gastrointestinal (GI) distress including nausea, vomiting, and/or abdominal pain are the most commonly reported adverse health effect in humans via oral exposure to copper due to its irritating property (ATSDR, 2004).

Given the role copper plays as an essential element to the human body, its ubiquitous nature in food and drinking water, and the lack of systemic toxicity resulting from copper, a quantitative toxicity assessment was not conducted for dietary, dermal, oral or inhalation exposures. It was concluded that "there are no risks of concern to the Agency" in the 2006 RED.

2.2 Endpoints/Points of Departure (PODs) for Risk Assessment

The current interim toxicological endpoints for silver in conducting hazard and risk assessments and PODs are based upon argyria, a permanent discoloration of the skin and/or eyes resulted in long-term exposure to silver. Argyria is believed to provide protection to individuals by preventing silver from entering circulation via oral, inhalation and dermal routes and being deposited in other body tissues.

For Inhalation Exposure, the Occupational Safety and Health Administration (OSHA) 8-hour time-weighted average (TWA) 0.01 mg/m^3 is used and an additional safety factor of 3x is applied to address the residual uncertainty associated with the missing 90-day inhalation toxicity, reproductive, neurotoxicity and chronic toxicology studies.

Oral exposure is not considered likely to result from the use of Tefcite. Although there is potential for dermal exposure, there is no dermal hazard, and therefore, no need to assess the dermal route.

The Agency has not selected toxicological endpoints for risk assessment for copper or zinc. Both copper and zinc are ubiquitous in the environment and are efficiently regulated in the human system. There is no evidence of systemic toxicity associated with copper and zinc exposure in pesticide use. Although endpoints for oral and dermal routes of exposure to silver were also available, these routes of exposure are not considered likely to result from the use of Tefcite.

2.3 Dietary Exposure Assessment

Dietary (food) exposures from Tefcite are not anticipated because the proposed use pattern does not include food uses (direct or indirect). Furthermore, dietary (drinking water) exposure is not expected for zinc or silver based on the low percent a.i. and resulting low concentrations in water. Although exposure to cuprous oxide is possible, there are no human health risks of concern and therefore, a drinking water assessment will not be conducted.

2.4 Residential (Non-Dietary) Assessment

Residential handler exposures are not anticipated because Tefcite will be applied as a powder coating using specialized equipment this is only available in a commercial setting. Powder coatings such as Tefcite cannot be applied using a brush or roller. Residential post application exposures are also not anticipated for antifoulant paints or coatings such as Tefcite because such paints and coatings are applied to the hull below the water line where there is minimal potential for human contact.

2.5 Occupational Exposure

Occupational handler exposures are anticipated during the application of the Tefcite coating. Although this coating is applied as a dry powder, rather than a typical antifoulant paint, which is applied a liquid, the process of application is similar in that it is sprayed. It should be noted; however, that the Tefcite powder particles are somewhat smaller than airless sprayer aerosols. According to Burgess, 1995, the particle distribution for airless spraying is wide with the majority of the mist particles in the 100 to 500 micron range. This is somewhat larger than the particle size distribution of Tefcite, which has a particle size distribution of 0.25 to 126 microns that consists of two populations (MRID 48858402). Population 1, which consists of 20.7% of the product, ranges from 0.25 to 20.0 microns with a peak of 13 microns while Population 2, which consists of 79.3% of the product, ranges from 20 to 126 microns with a peak of 63 microns.

Because there are no exposure data available for the application of antifoulant powder coatings, the exposure data that are available for the application of antifoulant paints using airless sprayers will be used as a surrogate with the understanding that the Tefcite powder has a somewhat smaller particle size than the airless sprayer aerosols.

2.5.1 Occupational Exposure Data

There are two exposure studies that measured occupational antifoulant painter exposures. These studies include MRID 467070-01 (i.e. the ZPT study) and MRID 489452-02 (i.e. the TNO study). The ZPT study is a proprietary study that measured zinc pyrithione exposures during the painting of ships in North America and the TNO study is an open literature study (Van Hemmen, 2006) that that measured copper exposure during the painting of ships in the Netherlands.

2.5.1.1 The ZPT Study - Assessment of Potential Inhalation and Dermal Exposure to Zinc Pyrithione during Outdoor Painting of Ship Hulls with Commercial Antifoulant Paint Containing Zinc Omadine (MRID 467070-01)

The objective of this study was to quantify dermal and inhalation exposures during the spray application of antifouling paint to the hulls of commercial cargo and passenger ships. The ships were painted with an EPA registered paint formulation (#2693-187) that contained 3.80% zinc pyrithione (ZPT) and has a coverage of 130 ft^2 per gallon. Exposure monitoring was conducted at shipyards in Boston, Massachusetts (Trials A and D) and Freeport, Grand Bahama (Trials B and C). The Boston shipyard contained an excavated drydock and the Freeport shipyard contained a floating drydock. A total of 49 experienced workers in three job categories (pot man, spray man and line tender) participated in this study. The workers were monitored for 1-2 consecutive work cycles each over one or two test days and each work cycle consisted of the application of one coat of paint. One to three crews were monitored during each work cycle and each crew consisted of one to two members of each job category. Painting was done with airless spray guns without wands, fed by high-pressure hoses from compressed air pumps operating at 3,500-4,500 pounds per square inch (psi). The work cycle durations ranged from 57 to 412 minutes and the surface area painted per person ranged from 5,000 to 13,800 ft^2. A summary of the conditions of each trial is given in Table 1.

Table 1 ZPT Study Shipyard Conditions

Trial	Ship Type	Date	Site Characteristics	Notes
A	Cruise Ship, 680' long, 91' beam, 20' draft	Nov-04	Plastic Sheeting with Some Gaps	Entire Hull below waterline was painted (27,600 ft^2) with two coats. One coat was applied each day. Each day was a work cycle. Workers wore work gloves with rubberized palms.
B	Mega Yacht, 171' long, 32' beam, 10' draft	Jan-05	Plastic Tenting with Small Exhaust Fan	Entire hull below waterline was painted (6400 ft^2) with three coats. One coat was on day one and two coats were applied on day two. Each coat was a work cycle. Workers wore nitrile gloves.
C	Cargo Ship, 90' long, 33' beam, 14' draft	Feb-05	No sheeting or tenting used	Same Yard as Trial B. Hull area = 5000 ft^2. Two coats were applied: one in the early afternoon and one in the evening. Each coat was a work cycle. Spray men also did line tending. Workers wore nitrile gloves.
D	Cruise Ship, 614' long, 92.5' beam, 20' draft	Apr-05	Plastic Sheeting with more gaps than trial A.	Narrow band at waterline painted (6800 ft^2) with two coats over two days. Each coat was a work cycle. Workers wore nitrile gloves.

Inhalation exposure was monitored using 37-mm glass fiber filters in closed face cassettes positioned in the breathing zone with a pump flow rate of 1.5 liters per minute.

The samples were collected, handled and analyzed in accordance with validated methods as described in the study report. Field and laboratory fortification samples were generated at two levels (2X LOQ and 150X LOQ) for each matrix. The results of the field fortification samples indicated that the recoveries were generally above 90% and that the fortification levels matched the dosimeter residue levels.

A summary of the inhalation exposure data is given in Table 2. The inhalation exposures are expressed as time weighted average (TWA) air concentrations and include all of the samples collected on a worker for a workday. During Trials A and D, only one sample was collected per worker per day and during Trials B and C one or two samples per worker per day were collected. The TWA is calculated using the following formula:

$$TWA = \frac{(\text{Sample Time\#1} * \text{Air Concentration\#1}) + (\text{Sample Time\#2} * \text{Air Concentration\#2})}{(\text{Sample Time\#1} + \text{Sample Time\#2})}$$

To provide a basis for comparison to the POD for silver, eight hour TWAs were calculated by assuming that ZPT exposure occurred only during the time of sampling. The maximum inhalation exposures occurred during Trial B when the work area was enclosed with plastic sheeting to contain overspray.

Table 2 ZPT Shipyard Study Inhalation Exposures (μg/m³)

Trial	Job	n	Sample Duration (Minutes)		Amount Ai Handled (lb)		ZPT TWA (μg/m³)		ZPT 8 Hour TWA (μg/m³)	
			Range	AVG	Range	AVG	Range	AVG	Range	AVG
A	SM	6	254-375	299	7.5-39.2	24.5	22.2 – 120	75.7	12.5 – 72.9	46
	LT	5	262-412	343	9.5-24.4	16.8	24.3 – 434	134	13.4 – 353	106
	PM	5	267-365	325	29.2-40.6	37.2	13.9 – 23.1	18.5	10.1 – 14.0	12.3
B	SM	4	101-130	116	6.97 -16.68	9.7	3812- 6333	5274	1033 – 1715	1263
	LT	4	101-130	116	8.95-14.57	11.8	141-2074	756	51- 481	190
	PM	2	101,130	116	17.9,29.1	23.5	105,118	112	22.1,32.1	27.1
C	SM	1	138	NA	20.4	N/A	396	NA	114	NA
	LT	1	138	NA	20.4	N/A	56.7	NA	16.3	NA
	PM	1	138	NA	20.4	N/A	50.4	NA	14.5	NA
D	SM	4	157-203	182	5.7-10.2	8.5	21.7-95.5	68.5	8.3 - 36.2	26.0
	LT	3	92-211	164	8.3-10.2	9.4	1.1-10.1	4.7	0.48 - 4.0	1.7
	PM	5	151-214	187	15.5-18.5	17.3	0.7-1.7	1.1	0.24 - 0.70	0.45

Job: SM = Spray Man, **LT** = Line Tender, **PM** = Pot Man

A statistical analysis of the unit exposure data was conducted to determine which unit exposure is the most representative of the range of exposures that would occur when spray painting ships (ICF, 2013). This analysis considered various combinations of the data from each Trial and used two models to calculate arithmetic means, confidence intervals and 95th percentile values for the three jobs. A summary of the results of this analysis is given in Table 3.

Table 3 ZPT Shipyard Study Inhalation Unit Exposure Statistical Analysis

Trial	Job	n	Inhalation Unit Exposure (μg/m³/lb ai)				
			AMs	AMm	K	AMm 95thCI	P95m
A	Spray Man	6	2.70	2.85	2.2	6.37	8.37
	Line Tender	5	6.15	5.31	2.4	12.7	15.6
	Pot Man	5	0.33	0.50	2.4	1.20	1.46
B	Spray Man	4	113	**149**	2.3	347	396
	Line Tender	4	15.1	**12.7**	2.3	28.7	33.6
	Pot Man	2	1.17	**1.57**	3.1	4.73	4.18
C	Spray Man	1	5.58				
	Line Tender	1	0.80				
	Pot Man	1	0.70				

Trial	Job	n	Inhalation Unit Exposure (µg/m³/lb ai)				
			AMs	AMm	K	AMm 95thCI	P95m
D	Spray Man	4	2.87	3.31	1.9	6.42	7.67
	Line Tender	3	0.17	0.13	2.1	0.28	0.31
	Pot Man	5	0.03	0.03	1.8	0.05	0.07
ABCD	Spray Man	15	32.5	48.6	34	1660	177
	Line Tender	13	7.10	12.0	33	402	43.9
	Pot Man	13	0.37	1.79	35	62.3	6.53
ACD	Spray Man	11	3.03	**8.27**	8.9	73.8	31.8
	Line Tender	9	3.56	**3.12**	8.9	27.6	12.0
	Pot Man	11	0.23	**0.44**	8.7	3.81	1.68

AMs = Arithmetic mean calculated using empirical simple random sampling model.
AMm = Arithmetic mean calculated using a lognormal mixed model.
AMm 95th CI = 95th Upper Confidence Limit on the AMm calculated using a lognormal mixed model.
P95m = 95th percentile calculated using a lognormal mixed model.

Based on the above analysis and given the conditions of each trial, the arithmetic mean for trial B and trails ACD and were selected to represent the range of shipyard worker exposures.

To be consistent with ongoing work of the Antimicrobial Exposure Assessment Task Force, the arithmetic mean that was calculated using the lognormal mixed model was selected to be used in risk assessment; however, it is acknowledged that k factor for trials ACD is above the recommended value of 3.

2.5.1.2 The TNO study - Occupational Exposure during Application and Removal of Antifoulant Paints (MRID 489452-02)

This study was conduct by the TNO, which is an independent research organization of the Netherlands, and it was published in the literature (Van Hemmen, 2006). The objective of this study was to quantify primary and secondary occupational exposures during the roller and spray application and sand blasting removal of antifouling paint. Both primary exposure (rolling and spraying) and secondary exposure (during sand blasting) were studied. Exposure during rolling was measured in boatyards where paints containing dichlofluanid (DCF) were applied. Spraying was measured in three dockyards (i.e. sites) in the Netherlands where paints containing copper were applied. During the spraying part of the study usually one large boat or two small vessels were present in the dockyard. All of the entrances to the dockyard were closed and mechanically ventilated with outside air. The paint sprayers often worked in pairs, e.g. one worked the upper part while the other worked on the bottom side, or one on port side and the other on starboard side. A spray gun or lance was used with a type 23.40 or 26.40 nozzle. Spraying was conducted from a tower wagon to cover the sides of the hull and from the floor to cover the bottom of the hull. Overhead spraying occurred regularly when spraying from the floor.

Fourteen workers participated in the spraying portion of this study and exposures were measured 12 times for sprayers and 10 times for potmen. The workers were sampled repeatedly. Inhalation exposure to copper was monitored using two 25 mm glass fiber filters in IOM samplers at a flow rate of 2.0 liters per minute. A bulk sample of the paint product (20–50 ml) was also taken on each sampling day.

The chemical analytical method for the determination of copper on the different matrices was validated with respect to linearity, repeatability, limit of detection and limit of quantification. No air aspiration tests were performed. An amount of diluted nitric acid (1 mol per liter) was added to the samples, so that the total sample was covered with nitric acid. The bottles were heated at 60 C for one hour and after shaking for 10 min, copper was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). Calibration samples were prepared by adding different concentrations of a commercial copper standard solution of 1000 mg per liter with diluted nitric acid. The method was validated with respect to the linearity (R-squared 0.999), recovery from spiked samples (range 80–120%), within-day and between days repeatability, limit of detection and limit of quantification.

A summary of the inhalation exposure data is given in Table 4. The paint used for spraying contained an average of 36 percent copper by weight with a range of 31.1 to 39.3 percent. The duration of painting varied between 66 and 151 minutes with a mean of 102 minutes. The average amount of paint used was 218 kg (range 108–347 kg, n = 11). This is about 120 liters of paint (or 32 gallons). Because of the data is reported only in summary form, it was not possible to do a statistical analysis as was done for the ZPT study.

Table 4 TNO Shipyard Study Inhalation Exposures to Copper

Scenario	N	Range (ug/m^3)	Geometric Mean (µg/m^3)	GSD	Arithmetic Mean (µg/m^3)	90th Percentile (µg/m^3)
Spray Painting	12	260 to 9,003	2,100	2.6	3,000	5,460
Paint Filling	10	120 to 2,470	650	2.9	1020	2,450

2.5.2 Occupational Exposure and Dose Calculations

2.5.2.1 Based on the ZPT Study

The inhalation exposures were calculated as air concentrations based on the ZPT study for comparison to the POD for silver using the average 8 hour TWAs for each trial/job combination. These TWAs were adjusted to account for the amount of a.i. present in the paint used in the ZPT study.

$$MOE = POD\ (mg/m^3)\ /\ 8\ Hour\ TWA\ (mg/m^3)$$

Where:

MOE	=	Margin of Exposure
POD	=	Point of Departure (0.01 mg/m^3)
TWA	=	Time Weight Average Air Concentration

2.5.2.2 Based on the TNO Study

The inhalation exposures were also calculated as air concentrations based on the TNO study; however, it was assumed that the 8 hour time weighted average exposure would be the same as the reported exposure. This is because the samples were fairly short (60 to 120 minutes) and it is not known what the workers did for the rest of the workday. In addition, it was necessary to normalize the exposure data by the average copper content of the paint because the study report only lists summary statistics for the exposures and copper content.

2.5.3 Occupational Exposure Assumptions

The following assumptions were used:

- The proposed paint contains 0.018 percent by weight silver. This value was used to adjust the air concentrations from the ZPT and TNO studies where the paint contained 3.8 percent ZPT and 36 percent copper, respectively.

- The amount of coating applied per day would be the same as was applied in the ZPT and TNO exposure studies.

- The label indicates that a forced air respirator should be worn. It is assumed that this would consist of a loose fitting hood (LFH) connected to a positive pressure air supply. This respirator provides a protection factor of 25 when properly used.

2.5.4 Occupational Exposure Risk Summary

2.5.4.1 MOEs based on the ZPT Study

A summary of silver inhalation MOEs for shipyard painters based on the ZPT study is included in Table 5. One MOE is of concern if no respiratory protection is worn. If PF25 respirators are worn, none of the MOEs are of concern.

Table 5 Inhalation MOEs for Silver (Ag) based on the ZPT Study

Job	n	Unit Exposure[A] ($\mu g/m^3$/lb ai)	LB a.i. Handled in ZPT Study[B]	LB Ag Handled When Applying Tefcite[C]	Ag Inhalation Exposure ($\mu g/m^3$)	Ag MOE[D]	
						No Resp.[E]	PF 25 Resp[F]
Trial A, C and D Combined							
Spray Man	11	8.27	23.8	0.113	0.93	11	340
Line Tender	9	3.12	8.9	0.042	0.13	77	250
Pot Man	11	0.44	28.9	0.137	0.060	170	1200
Trial B							
Spray Man	4	149	9.7	0.046	6.85	**1.5**	36
Line Tender	4	12.7	11.8	0.056	0.71	14	350
Pot Man	2	1.57	23.5	0.111	0.17	59	1500

***MOEs highlighted in bold font are of concern because they are less than the target MOE of 3**

A. Arithmetic mean 8 hour TWA from the ZPT shipyard study calculated using the lognormal mixed model.

B. Arithmetic mean calculated directly.

C. Lb ai handled during the ZPT study adjusted for the silver content of Tefcite (0.018 % Ag in Tefcite / 3.8% ZPT in study)

D. Inhalation MOE for Ag = POD (0.01 mg/m^3 or 10 $\mu g/m^3$) / Inhalation Exposure ($\mu g/m^3$)

E. No Resp. means that MOEs were calculated assuming that no respirators are worn.

F. PF25 Resp. means a loose fitting hood positive pressure respirator that provides a protection factor of 25.

2.5.4.2 MOEs based on the TNO Study

A summary of silver inhalation MOEs for Tefcite shipyard painters based on the TNO study is included in Table 6. None of the MOEs are of concern.

Table 6 Inhalation MOEs for Silver (Ag) based on the TNO Study

Exposure Scenario[A]	Copper 8 Hour TWA[B]	Ag Adjusted 8 hour TWA[C] ($\mu g/m^3$)	Ag Inhalation MOE[D] (Target MOE = 3)	
			No Respirator[E]	PF25 Respirator[F]
Spray Painters	3,000 $\mu g/m^3$	1.5 $\mu g/m^3$	6.7	170
Paint Fillers	1020 $\mu g/m^3$	0.51 $\mu g/m^3$	20	500

A. The TNO study only lists summary statistics for the exposures and the copper content of the paint; therefore, the unit exposures was estimated by using average exposure.
B. Copper exposure ($\mu g/m^3$ as an 8 hour TWA)
C. Adjusted 8 Hour TWA for Ag = Copper 8 Hour TWA * (0.018 % Ag in proposed paint/36% in copper paint)
D. Inhalation MOE for Ag = POD (0.01 mg/m^3 or 10 $\mu g/m^3$)/ Adjusted 8 Hour TWA ($\mu g/m^3$)
E. No Resp. means that MOEs were calculated assuming that no respirators are worn.
F. PF25 Resp. PF25 Resp. means a loose fitting hood positive pressure respirator that provides a protection factor of 25.

2.5.5 Occupational Exposure Conclusions

The MOEs were calculated for inhalation to silver in the proposed Tefcite coating using both data from the ZPT study and from the TNO study. If no respiratory protection is worn, one MOE is of concern, when using the ZPT data and no MOEs are of concern when using the TNO data. If PF25 respirators are worn as required by the label, none of the MOEs are of concern.

Because copper has been previously been registered as an antifoulant, exposures to copper were not evaluated for the registration of Tefcite. It should be noted; however, that the two studies considered in the review of the silver exposures and the high copper content of Tefcite coating suggest that copper exposures could exceed the OSHA PEL of 1.0 mg/m^3 for copper dust. It is recommended that the respirators be worn as required by the label to reduce the copper exposures to below the OSHA PEL.

2.5.6 Human Studies Considerations

Both of the exposure studies mentioned in this risk assessment have been cleared for use in risk assessment by the OPP ethics reviewers.

3 Ecological Risk Assessment

The ecological risk for each one of the three active ingredient components were evaluated in this assessment.

3.1 Conceptual Exposure Model

Boats and structures treated with Tefcite are expected to leach copper, silver, and zinc into water in which treated boats and structures reside. Potential significant exposure pathways to aquatic animals include: 1) uptake across gills and across their integuments from the water column or pore water; and 2) ingestion by benthic organisms or filter feeders of metals sorbed to solids in the sediment or water column. The inorganic metallic forms of metal that would be released from Tefcite have not been reported to form methylated complexes or other organic complexes that would be of concern for bioaccumulation in the food chain. At natural levels of these metals in the environment, food-chain biomagnification has generally not been found to be a problem. Both zinc and copper are essential elements and even when higher levels are accumulated or adsorbed in components of lower trophic levels (e.g., algae), homeostasis mechanisms tend to compensate. Silver is not an essential element for organisms. In metal enriched environments, bioaccumulation factors in bivalves such as oysters and scallops have been reported for silver to be around 18,700 and 2,300, respectively, similarly sorption to phytoplankton results in high bioaccumulation factors for silver, whereas in fish factors are generally <1000 (USEPA 1987a). While the agency recognizes that enrichment may occur in certain trophic levels, no quantitative risk assessment of the food chain exposure pathway was performed to address risk to terrestrial animals from this exposure route.

3.2 Exposure Assessment

3.2.1 Fate and Transport Processes

3.2.1.1 Summary of Abiotic Environmental Fate Processes

These metals will leach from treated boat paint into water with maximum leach rates of 71.6, 1.9, and 1.5 ug/cm^2/day for copper, zinc, and silver, respectively (MRID 48772001). While the speciation of copper reported for leaching was not reported, any cuprous (Cu^{1+}) ion that leaches into the aquatic environment should undergo oxidation to form cupric (Cu^{2+}) ions. The metals themselves do not degrade by hydrolysis or photodegradation which are abiotic dissipation routes.

Sorption is the dominant environmental process affecting copper, zinc, and silver availability in the aquatic environment. Also, these metal ions can form complexes with negatively-charged ions and undergo reduction and oxidation (redox) reactions. The abiotic environmental parameters that control metal availability include pH, water hardness, salinity, and concentration of organic matter. Aquatic toxicity of these metals is influenced by a number of these same factors (U.S. EPA 1987[1], U.S. EPA 1995 aquatic water quality criteria (AWQC) documents[2], U.S. EPA 2007[3]). The MAMPEC model incorporated all of these parameters except for hardness, which is accounted for by adjusting salinity.

3.2.1.2 Summary of Biotic Environmental Fate Processes

Cuprous oxide, and metallic silver and zinc are inorganic compounds and metals that do not undergo biological degradation or mineralization, and therefore are not affected by metabolic degradation. As a result, the agency did not incorporate any biological degradation in the MAMPEC modeling. However, copper and zinc are both essential nutrients and components of enzymes and metalloproteins. Once released from treated paint, copper and zinc will form organic complexes and sorb to organic matter in the water column and sediment.

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[1] USEPA 1987 http://yosemite.epa.gov/water/owrccatalog.nsf/065ca07e299b464685256ce50075c11a/149dcbd15563dfca85256b060072309c?OpenDocument&CartID=null

[2] USEPA 1995 http://yosemite.epa.gov/water/owrccatalog.nsf/065ca07e299b464685256ce50075c11a/0b272603b228926785256d83004fd9ee?OpenDocument&CartID=null

[3] USEPA 2007 http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/copper/2007_index.cfm

3.2.1.3 Summary of Environmental Transport Processes

Once leached from treated boat paint, the fate of all three of these metals (copper, zinc, and silver) are dominated by precipitation and dissolution of mineral phases and the formation of complexes with other sediment solution constituents. These constituents include water, and hydroxyl ions, but also sulfides, nitrate, and chloride. Neutral organics and organic acids also complex metals in the sediment. On the other hand, the sorption of silver is not a function of pH, but is a function of ligands (organic molecules) in the environment. The extent of sediment sorption of these compounds was accounted for in MAMPEC by use of a Kd value and the effect of pH was addressed using a pH of 7 in freshwater and a pH of 8 in salt water. Table 27 in Appendix B contains all the sorption values for these values in MAMPEC modeling.

3.2.1.4 Summary of Biotic Environmental Fate Processes

Cuprous oxide, and metallic silver and zinc oxide are inorganic compounds and metals that do not undergo biological degradation. Therefore, they are not affected by metabolism. However, copper and zinc are both essential nutrients and components of enzymes and metalloproteins. Released metals will form organic complexes and sorb to organic matter in the water column and sediment and the agency is considering the effect or organic matter in MAMPEC modeling. Table 27 and Table 28 of Appendix B contains the input parameters for MAMPEC for all three metals.

3.2.2 Summary of Estimated Environmental Concentrations in Water

Tefcite is intended to be used for mollusk control on the bottom and sides of treated boats and ships. Once the boats or ships are in the water, the metal oxide active ingredient or metal cations are expected to leach continuously below the water line into the adjacent surface waters. To quantify emissions and estimate concentrations of these metals in surface water, sediment, and particulate matter to which aquatic life may be exposed, the agency used the marine antifoulant model and software package MAMPEC (Version 3).[4] MAMPEC is an integrated hydrodynamic and chemical fate model which is used as a tool to predict the estimated concentrations for exposure assessment of antifoulants in marinas, harbors, rivers, estuaries and open waters. MAMPEC was originally developed by the Institute of Environmental Studies (Instituut voor Milieuvraagstukken, IVM), Free University (Vrije Universiteit, VU) of Amsterdam and Delft Hydraulics for the Antifoulant Working Group (AFWG) of the European Paint Makers Association (CEPE) in 1999, several updates have since been made.

The model provides prediction of environmental concentrations of antifouling products in six generalized "typical" marine environments (commercial harbor, estuarine harbor, marina, marina poorly flushed, open sea, and shipping lane). The model is also used for exposure assessment in freshwater systems and discharges of chemicals in ballast water. There are three types of inputs: 1) environmental parameters (hydrodynamics, water characteristics, etc. of the scenario); 2) emission parameters (sizes, numbers, surface area, leach rate, etc.); and 3) compound-specific inputs. Except for the leach rate and compound-specific inputs, the agency has been using the

[4] http://www.deltares.nl/en/software/1039844/mampec/1232321

standard OECD-EU scenarios (ESD-PT21) for environment and emission inputs for marine environments (van de Plassche and van deer Aa, 2004).

For the current modeling effort, the Agency conducted modeling for two freshwater marinas, including an inland marina (poorly-flushed) containing 75 boats and a Swiss Marina (containing 299 boats. The saltwater environments modeled included a commercial harbor (136 boats) and the default marina (299 boats). MAMPEC does not include hardness as an input, and as a result, salinity was used as a surrogate for hardness in the fresh water scenarios. To run the default marina as an inland freshwater scenario, the salinity was modified to 0.035 parts-per-thousand (ppt) and the pH was adjusted to 7 (unitless). The leaching rates from treated paint in MRID 48772001 were used as inputs for the model. The maximum leaching rate for copper (71.6 μg/cm^2/day) is 38X and 48X the leach rates for zinc (1.9 μg/cm^2/day) and silver (1.5 μg/cm^2/day), respectively. Appendix B contains additional details on the scenarios and inputs to the model.

The MAMPEC version 3.0 (v3.0) model was used to estimate the surface water concentrations of each metal separately. MAMPEC predictions include maximum, 95th percentile, median, average, and minimum estimates of exposures. For this screening assessment, the maximum concentration was used for evaluating acute effects to aquatic organisms, the average exposure estimate is used for evaluating chronic effects and effects to aquatic plants, and the minimum exposure concentration was used in risk characterization. MAMPEC predictions among active ingredients for all scenarios were essentially proportional to the leaching rate with the copper:zinc ratio of 36-38X and a copper:silver ratio of 46-48X. Table 7, Table 8, Table 9, and Table 10 contains the EECs for dissolved copper, zinc, and silver from the use in Tefcite in a freshwater inland marina (poorly-flushed) containing 75 boats, a freshwater Swiss Marina (containing 299 boats), a saltwater commercial harbor (136 boats), and a saltwater default marina (299 boats), respectively. Appendix B contains additional details on model inputs and results.

Table 7 Estimated Environmental Concentrations of Copper, Zinc, and Silver in a Small, Freshwater Inland Marina Containing Soft Water and 75 Boats.

Compound		Total concentration (μg/l)	Dissolved (μg/l)	Suspended solid (μg/g dry weight)	Sediment after one year (μg/g) dry weight
Copper (maximum leaching rate in μg/cm^2/day)	Maximum concentration	61.1	60.2	24.1	2.9
	Average concentration	37.8	37.3	14.9	1.8
	Minimum concentration	13.0	12.8	5.1	0.61
Zinc (maximum leaching rate in μg/cm^2/day)	Maximum concentration	1.6	1.6	0.044	0.0053
	Average concentration	1.0	1.0	0.027	0.0032
	Minimum concentration	0.35	0.35	0.0093	0.0011
Silver (maximum leaching rate in μg/cm^2/day)	Maximum concentration	1.3	1.3	0.0046	0.00055
	Average concentration	0.80	0.80	0.0029	0.00034
	Minimum concentration	0.27	0.27	0.00098	0.00012

Table 8 Estimated Environmental Concentrations of Copper, Zinc, and Silver in an Inland Marina Freshwater Marina Containing Soft Water and 299 Boats.

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Copper (maximum leaching rate in µg/cm²/day)	Maximum concentration	184	182	72.7	8.7
	Average	126	124	49.8	6.0
	Minimum concentration	62.8	61.9	24.8	3.0
Zinc (maximum leaching rate in µg/cm²/day)	Maximum concentration	5.1	5.1	0.14	0.017
	Average concentration	3.5	3.5	0.095	0.11
	Minimum concentration	1.8	1.8	0.048	0.0057
Silver (maximum leaching rate in µg/cm²/day)	Maximum concentration	4.0	4.0	0.015	0.0017
	Average concentration	2.8	2.8	0.010	0.0012
	Minimum concentration	1.4	1.4	0.0050	0.00060

Table 9 Estimated Environmental Concentrations of Copper, Zinc, and Silver in a Saltwater Commercial Harbor.

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Copper (maximum leaching rate in µg/cm²/day)	Maximum concentration	32.8	32.4	0.80	1.6
	Average concentration	11.7	11.5	0.29	0.56
	Minimum concentration	0.46	0.45	0.011	0.022
Zinc (maximum leaching rate in µg/cm²/day)	Maximum concentration	0.88	0.87	0.024	0.0015
	Average concentration	0.31	0.31	0.0084	0.00052
	Minimum concentration	0.012	0.012	0.00033	0.000020
Silver (maximum leaching rate in µg/cm²/day)	Maximum concentration	0.69	0.69	0.0025	0.00015
	Average concentration	0.25	0.25	0.00089	0.000055
	Minimum concentration	0.0095	0.0095	0.000034	0.0000021

Table 10 Estimated Environmental Concentrations of Copper, Zinc, and Silver in a Saltwater Default Marina.

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Copper (maximum leaching rate in µg/cm²/day)	Maximum concentration	115	113	45.2	5.4
	Average concentration	79.3	78.2	31.3	3.8
	Minimum concentration	39.0	38.0	15.2	1.8
Zinc (maximum leaching rate in µg/cm²/day)	Maximum concentration	3.1	3.1	0.084	0.010
	Average concentration	2.2	2.2	0.059	0.0070
	Minimum concentration	1.1	1.1	0.029	0.0034
Silver (maximum leaching rate in µg/cm²/day)	Maximum concentration	2.5	2.5	0.0089	0.0011
	Average concentration	1.7	1.7	0.0062	0.00074
	Minimum concentration	0.84	0.84	0.0030	0.00036

3.2.2.1 Water Quality

Copper, silver and zinc are identified as the causes of impairment for several types of surface waters under section 303(d) of the Clean Water Act[5]. The amount of area reported as impacted for assessed waters are summarized in Table 11. There are a variety of specific causes of impairment due to metals and they include factories, mining, runoff from urban areas, antifoulant paint, as well as natural processes such as erosion of soil and rocks (USEPA 2012b;).

Total Maximum Daily Loads (TMDL) have been developed for copper with antifoulant paint as the impairment source in at least three locations[6]: Marina Del Rey in Los Angeles, California; Shelter Island Yacht Basin in San Diego Bay, California; and Newport Bay in Orange County, California. More information on impaired water bodies and TMDLs can be found at EPA's website[7]. There are a number of other marinas where copper has been identified as exceeding water quality criteria. The California Environmental Protection Agency, Department of Pesticide Regulation (DPR) sampled water and sediment from 23 California marinas in the summer and fall of 2006 to assess pollution stemming from the use of antifouling paint pesticides (Singhasemanon, Pyatt and Bacey 2009). Both saltwater and freshwater marinas were included in the monitoring program and both copper and zinc were measured at these sites. Singhasemanon, Pyatt, and Bacey (2009) reported that the highest dissolved copper concentrations were observed in larger salt water marinas along California's Central and South Coast and that the lowest were seen in freshwater lake marinas. Singhasemanon, Pyatt, and Bacey (2009) also

[5] http://ofmpub.epa.gov/tmdl_waters10/attains_nation_cy.cause_detail?p_cause_group_name=METALS (OTHER THAN MERCURY)
[6] http://ofmpub.epa.gov/tmdl_waters10/attains_impaired_waters.tmdls?p_pollutant_id=345
[7] http://www.epa.gov/owow/tmdl/

stated that: "Copper and zinc concentrations were almost always higher in the marinas than in the adjacent local reference sites, indicating that significant sources of metals existed in the marinas. Concentrations of zinc never exceeded California's water quality standards. In contrast, concentrations of dissolved copper in salt and brackish water marinas were frequently above California water quality standards established for the protection of aquatic life." A freshwater and saltwater biotic ligand model (BLM) and a Dissolved Organic Carbon Model were used to calculate site specific copper toxicity. The state of California has proposed banning the use of copper antifoulant paint on pleasure craft. In May 2011, the state of Washington signed into law the phase-out of copper-based bottom paint for recreational boats under 65 feet (2011-Senate Bill 5436[8]). Johnson and Gonzlez (2005) reported at a conference that internationally, copper-based paints have been banned for pleasure craft on the east coast of Sweden, restricted on the west coast of Sweden and in Denmark, and banned in the Netherlands.

Table 11 Identified Area of Assessed Waters Impaired under 303(d) of the Clean Water Act due to Copper, Silver, and Zinc

Cause of Impairment	Size of Assessed Waters with Listed Causes of Impairment					
	Rivers and Streams (miles)	Lakes, Reservoirs, and Ponds (acres)	Bays and Estuaries (square miles)	Coastal Shoreline (miles)	Ocean and Near Coast (square miles)	Wetlands (acres)
Copper	12,888	37,135	983	52	14	<1
Contaminated Sediments (Copper)			1			
Silver	907	18,085	<1		13	
Contaminated Sediments (Silver)			<1			
Zinc	6,839	34,075	11		14	<1
Contaminated Sediments (Zinc)	2		2			<1

Source: http://ofmpub.epa.gov/tmdl_waters10/attains_nation_cy.cause_detail?p_cause_group_name=METALS (OTHER THAN MERCURY), obtained as of May 5, 2014

3.3 Ecological Risk Characterization

3.3.1 Risk Estimation

Risk estimation integrates the results of exposure and stressor-response data to evaluate the likelihood of adverse ecological effects. For this risk assessment the risk quotient (RQ) method was used for estimating risks. In the RQ method, estimates of exposure are divided by ecotoxicity endpoint values. These RQs are then compared to presumptive levels of concern (LOCs) to identify potential risk to nontarget organisms and the need to consider regulatory action. These LOCs are standards used by the EPA to indicate potential risk to non-target organisms and the need to consider regulatory action; the development of these LOCs are discussed in detail in the Agency's Overview Document[9]. Types of RQs (e.g., acute versus chronic), RQ equations, and corresponding LOCs and risk presumptions are tabulated

[8] http://www.washingtonvotes.org/2011-SB-5436

[9] http://www.epa.gov/espp/consultation/ecorisk-overview.pdf

in Table 12. Exposure models and estimates are discussed in Section 3.2.2. Stressor-response endpoints used in risk estimation are discussed in Section 3.3.1.1.

Table 12 RQ Equations, LOCs and Risk Presumption Categories

Risk Presumption for Terrestrial Animals	RQ	LOC
Acute: Presumption of high acute risk for nontarget animals	EEC^A/LC_{50} or EEC^B/LD_{50}	≥ 0.5
Acute Endangered Species: Endangered species may be affected	EEC^A/LC_{50} or EEC^B/LD_{50}	≥ 0.05
Chronic Risk: Presumption of chronic risk to nontarget animals, endangered species may be affected chronically	$EEC^C/NOAEC$	> 1.0
Risk Presumption for Aquatic Animals	**RQ**	**LOC**
Acute: Presumption of high acute risk for nontarget animals	EEC^D/LC_{50} or EEC^D/EC_{50} or EEC^D/IC_{50}	≥ 0.5
Acute Endangered Species: Endangered species may be affected acutely	EEC^D/LC_{50} or EEC^D/EC_{50} or EEC^D/IC_{50}	≥ 0.05
Chronic Risk: Presumption of chronic risk to nontarget animals, endangered species may be affected chronically	Water: $EEC^E/NOAEC$	> 1.0
	Sediment: $EEC^F/NOAEC$	>1.0
Risk Presumption for Aquatic Plants	**RQ**	**LOC**
Non-Endangered Species: Presumption of high risk to all nontarget aquatic plants	EEC^G/IC_{50}	> 1.0
Endangered Species: Endangered plants may be affected	$EEC^G/NOAEC$ or $EEC^G/IC_{05}{}^H$	> 1.0
Risk Presumption for Terrestrial Plants	**RQ**	**LOC**
Non-Endangered Species: Presumption of high risk to all nontarget plants	EEC^I/IC_{25}	> 1.0
Endangered Species: Presumption of high risk to all nontarget aquatic plants	$EEC^I/NOAEC$ or $EEC^I/IC_{05}{}^H$	> 1.0

[A] Dietary acute exposure in parts per million (ppm) of the pesticide in/on dietary items.

[B] Dietary acute exposure dose in mg/kg-bw/day.

[C] Dietary chronic exposure in ppm of the pesticide in/on dietary items.

[D] Acute exposure concentration in water in ppm.

[E] Chronic exposure concentration in water in ppm.

[F] Chronic exposure concentration in mg/kg-sediment.

[G] Exposure concentration in water in ppm for aquatic plants.

[H] An IC_{05} can be used in lieu of an NOAEC, if a NOAEC cannot be determined or if it is above the IC_{25}.

[I] Exposure concentration in pounds per acre (lbs/A) for terrestrial applications or in ppm from assessment of water inundated exposures used in antimicrobial assessments.

3.3.1.1 Selected Ecological Toxicity Endpoints (Stressor-Response Profile)

Acute and chronic toxicity data from studies submitted by registrants along with public literature reviewed and included in U.S. ambient water quality criteria documents were used to evaluate the potential direct and indirect effects of copper, zinc and silver in Tefcite to aquatic and terrestrial receptors. For a screening assessment, the most sensitive study result for the measurement endpoints used (e.g., 96-hr LC_{50} values for acute risks for fish) are selected for calculating RQs. The agency included recommended national ambient water quality criteria (AWQC) values to the assessment to refine estimates.

Recently AD has added freshwater marina scenarios to assessment of antifoulant paints. In the case of metals this means the agency needs to consider the impact of water chemistry on the effect level for aquatic organisms but that such risks have also not been considered for most other antifoulant paints. Except for copper, freshwater criteria are based on hardness-dependent relationships which can be parameterized with relative ease to reflect national ranges. However, the current ambient water quality criterion method for developing acute copper criteria is based on a biotic ligand model and requires inputs for temperature, pH, dissolved organic carbon (DOC), major geochemical cations (calcium, magnesium, sodium, and potassium), dissolved inorganic carbon (the sum of dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate), and other major geochemical anions (chloride, sulfate) to convert toxicity values normalized to moderately-hard reconstituted water conditions to effect levels at other exposure conditions. Except for temperature, pH, and DOC, such factors are not included in the exposure model used for the ecological assessment, nor have they been parameterized for conducting a national assessment at this time. Therefore for assessing risks to the freshwater environment the previous copper hardness-dependent relationship was used to account for effects of water chemistry on toxicity. The impact of not using the biotic ligand method to estimates of risk is discussed in the risk characterization.

Most endpoints for aquatic organisms were derived from Office of Water's (OW's) ambient water quality criteria (AWQC) documents (USEPA 1980, 1985, 1987, 1995, 2007b). A discussion of the effects data and toxicity profile for each metal is provided in Appendix B. The most sensitive toxicity result for each receptor group was selected for conduct of the risk assessment. Because water chemistry can affect toxicity of metals, results were normalized to the same conditions before selection of the most sensitive test result. In some cases these values were provided within the criteria documents and in others while species mean acute values (SMAVs) were provided the individual study results were not. Therefore normalization was done prior to selection in these cases. For results used in development of hardness-dependent criteria, this meant normalization to a water hardness of 50 mg/L as $CaCO_3$. Selected endpoints for freshwater animals, saltwater animals and aquatic plants are provided in Tables 11, 12, and 13, respectively, for copper; Table 14, 15, and 16, respectively for silver; and Tables 17, 18, and 19, respectively, for zinc.

3.3.1.2 Risk Quotients (RQs)

RQs for aquatic organisms exposed to copper, silver and zinc leached from boats and ships treated with Tefcite for the freshwater inland marina scenarios are in Table 20, Table 22, and Table 24, respectively, and are in Table 21, Table 23, and Table 25 for the saltwater marina and commercial harbor scenarios, respectively.

For copper, acute and chronic RQs exceeded acute non-listed and chronic LOCs for both soft and hardwater conditions modeled for freshwater marinas, and for both the saltwater marina and commercial harbor. Acute RQs in the freshwater marinas ranged from 1.1 in the small, hardwater marina to 112 in the large, softwater marina. Chronic RQs in the freshwater marinas ranged from 2.5 in the small, hardwater marina to 210 in the large, softwater marina. Aquatic plant RQs ranged from <1 to 1.1 for non-listed vascular plants and 32 to 105 for non-listed, nonvasculars. The larger freshwater marina for both soft and hard water conditions had higher acute and chronic RQs, and aquatic plant RQs, than the smaller marina. In the saltwater marina, acute RQs ranged from 8.0 to 25, chronic RQs ranged from 17 to 25, and nonlisted aquatic plant RQs ranged from <1 to 66, with listed aquatic plant RQs ranging from 15 to 99. In the commercial harbor, acute RQs ranged from 2.3 to 7.0, chronic RQs ranged from 2.5 to 3.6, and nonlisted aquatic plant RQs ranged from <1 to 9.8, with listed aquatic plant RQs ranging from 2.3 to 15.

For silver, acute and chronic RQs exceeded acute non-listed and chronic LOCs for softwater conditions modeled for both the small and large freshwater marinas. The smaller marina located in hardwater conditions did not exceed acute non-listed, chronic LOCs, or aquatic plant listed and non-listed LOCs. The larger marina located in hardwater conditions had acute RQs that exceeded acute listed LOCs but not acute nonlisted LOCs, and had a chronic RQ (1.2) that just exceeded the chronic LOC (1.0). The saltwater marina exceeded acute and chronic LOCs, the non-listed aquatic plant LOC were not exceeded. The commercial harbor had acute RQs that exceeded the listed species acute LOC, and exceeded the chronic LOC. Acute RQs in the freshwater marinas ranged from 0.03 in the small, hardwater marina to 29 in the large, softwater marina. Chronic RQs in the freshwater marinas ranged from <1 in the small, hardwater marina to 200 in the large, softwater marina. Aquatic plant RQs were <1 for non-listed vascular plants and <1 to 1.1 for non-listed, nonvasculars. The larger freshwater marina for both soft and hard water conditions had higher acute and chronic RQs, and aquatic plant RQs, than the smaller marina. In the saltwater marina, acute RQs ranged from 0.22 to 3.2, chronic RQs ranged from 3.2 to 8.9, and nonlisted and listed aquatic plant RQs were all <1. In the commercial harbor, acute RQs ranged from 0.1 to 0.27, chronic RQs ranged from <1 to 1.4, and nonlisted nonvascular aquatic plant RQs ranged from <1 to 1.4. The listed vascular aquatic plant RQs could not be calculated because there was not an acceptable NOEC value for vascular aquatic plants.

For zinc there was no exceedance of non-listed acute or chronic LOCs or listed and non-listed plant LOCs for any of the freshwater marina scenarios, the saltwater marina, or commercial harbor scenarios. The freshwater marina in softwater conditions had exceedances of the listed species acute LOCs. Acute RQs in the freshwater marinas ranged from <0.01 in the small, hardwater marina to 0.41 in the large, softwater marina. Chronic RQs in the freshwater marinas were all <1. Aquatic plant RQs were <1 for both non-listed and listed vascular plants, and nonlisted nonvascular. There was no NOEC for nonvascular aquatic plants so an RQ could not be calculated. In the saltwater marina and commercial harbor, acute RQs ranged from <0.01 to 0.02, chronic RQs were <1, and aquatic plant RQs were <1.

Table 13 Effect Endpoints Selected for Assessing Risks from Copper to Freshwater Animals

Receptor Group	Representative Species	Risk Scenario	AWQC Pooled Slope[a]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[b,c,d]:			Adjusted Toxicity Value (ppb), as Dissolved[e], at Water Hardness:			Source
			m	h1	t1	x1	y1	15	50	286	15	50	286	
Freshwater Invertebrate	Cladoceran, *Ceriodaphnia reticulata*	Acute	0.9422	240	23	5.4806	3.1355	1.69	5.25	27.1	1.62	5.0	26	Lind et al. Manuscript (1978) as cited in USEPA 1995 [f]
		Chronic	0.8545	50	1.72	3.9120	0.5423	0.61	1.72	7.6	0.59	1.65	7.3	Estimated[j]
Freshwater Fish and Amphibians	Rainbow trout, *Oncorhynchus mykiss*	Acute	0.9422	366	70.0	5.9026	4.2485	3.45	10.73	55.5	3.31	10.3	53	Howarth & Sprague 1978 as cited in USEPA 1985. [f]
		Chronic	0.8545	50	3.52	3.9120	1.2585	1.26	3.52	15.6	1.21	3.38	15.0	Estimated[j]
5th Percentile Aquatic Animals	Species distribution, AWQC CMC[g]	Acute	0.9422	50	7.29	3.9120	1.9859	2.34	7.29	37.7	2.25	6.99	36.2	Hardness-based National Recommended WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm
	Species distribution, AWQC CCC[h]	Chronic	0.8545	50	5.16	3.9120	1.6408	1.84	5.16	22.9	1.77	4.95	22.0	

[a]The acute slope of 0.9422 and chronic slope of 0.8545 for hardness dependent criteria are from Appendix B of current Recommended National Ambient WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm.

[b]Natural log values of water hardness (x = Ln(hardness)) at 15, 76, 136, and 286 mg $CaCO_3$/L are 2.7080, 3.9120, 4.3307, 4.9126, and 5.6560, respectively.

[c]Adjusted toxicity value from point-slope linear relationship[y = m(x - x1) + y1]; see table footnote (b) for definition of x.

[d]Exp(y); see table footnote (c) for definition of y.

[e]Total recoverable values adjusted to dissolved using the conversion factor of 0.96 for acute and 0.83 for chronic from Appendix A of current Recommended National Ambient WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm.

[f] The lowest freshwater invertebrate and fish normalized (hardness of 50 mg/L as $CaCO_3$) acute toxicity values based on data in EPA 1985 and 1995.

[g]The hardness-based from Appendix B of current Recommended National Ambient WQC given as exp(0.9422*[ln(hardness)-1.700], based on USEPA 1995.

[h]The hardness-based CCC from Appendix B of current Recommended National Ambient WQC given as exp(0.08545*[ln(hardness)-1.702], based on USEPA 1995.

[i] Values were reported as dissolved metals so no additional conversion is required.

[j] Estimated using FACR of 3.05 (ACR of 3.22 from USEPA 2007b adjusted for use of NOEC rather than IC_{20} or MATC), applied to the normalized (hardness 50 mg/L as CaCO3) acute value and the pooled chronic slope.

Table 14 Effect Endpoints Selected for Assessing Risks from Copper to Saltwater Animals

Receptor Group	Representative Species[a,b]	Endpoint				Source
		Risk Scenario	Type	Toxicity Value, Total Recoverable (ppb)	Toxicity Value, Dissolved[c] (ppb)	
Saltwater fish	Summer flounder, *Paralichthys dentatus*	Acute	EC_{50}	11.9	9.88	Cardin, 1982 as cited in USEPA 1985 and by reference in USEPA 1995
		Chronic	NOAEC	3.9	3.2	Estimated[a]
Saltwater crustacean	Copepod, *Acartia tonsa*	Acute	96-h LC_{50}	17.0	14.1	Sonowski & Gentile, 1978 as cited in USEPA 1985 and by reference in USEPA 1995
		Chronic	NOAEC	5.6	4.6	Estimated[a]
Mollusk	Pacific oyster (embryo), *Crassostrea gigas*	Acute	IC_{50}	5.3	4.4	Martin, et al. 1981 as cited in USEPA 1985 and by reference in USEPA 1995
5th Percentile Aquatic Animals	Species Distribution: AWQC CMC	Acute	FAV/2	4.8	4.0	National Recommended WQC[b]
	Species Distribution: AWQC CCC	Chronic	MATC	3.1	2.6	

[a] Used FACR of 3.05 (ACR of 3.22 from USEPA 2007b adjusted for use of NOEC rather than IC_{20} or MATC).

[b] http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

Table 15 Effect Endpoints Selected for Assessing Risks from Copper, Silver and Zinc to Aquatic Plants

Receptor Group	Representative Species[a,b]	Endpoint				Source
		Risk Scenario	Type	Toxicity Value, Total Recoverable (ppb)	Toxicity Value, Dissolved[c] (ppb)	
Copper						
Nonvascular aquatic	Green alga, *Pseudokirchneriella subcapitata*	Non-listed species	4-day EC_{50}	1.2	--	MRID 43363603
		Listed species	NOAEC	0.8	--	
Vascular aquatic	Duckweed, *Lemna gibba*	Non-listed species	7-d EC_{50}	119	--	Walbridge 1977 as cited in USEPA 1985, 2007b
		Listed species	7-d NOEC	5.2	--	Used the EC_{50} to NOEC ratio from MRID 43363604 of 23 to estimate a NOEC

Receptor Group	Representative Species[a,b]	Endpoint				Source
		Risk Scenario	Type	Toxicity Value, Total Recoverable (ppb)	Toxicity Value, Dissolved[c] (ppb)	
Silver						
Nonvascular aquatic	Green algae	Non-listed species	4-day IC_{50}	2.6 ppb		USEPA 1987a
	Red alga, *Champia parvula*	Listed species	28-d NOAEC	1.2	--	USEPA 1987a
Vascular aquatic	Duckweed, *Lemna minor*	Non-listed species	28-d IC_{50}	270 ppb	--	Brown and Rattigan 1979 as cited in USEPA 1987a
		Listed species	NOEC	No data		
Zinc						
Nonvascular aquatic	Saltwater diatom, *Schroederelia schroederi*	Non-listed species	4-day IC_{50}	19	--	Kayser 1977 as cited in USEPA 1987b
		Listed species	NOAEC	No value reported		
Vascular aquatic	Duckweed, *Lemna minor*	Non-listed species	4-d IC_{50}	10,000 ppb	--	Wang 1986 as cited in USEPA 1987b
		Listed species	70-d NOEC	$\geq$654 ppb		Van der Werff and Pruyt 1982 as cited in USEPA 1987b

Table 16 Effect Endpoints Selected for Assessing Risks from Silver to Freshwater Animals

Receptor Group	Representative Species	Risk Scenario	AWQC Pooled Slope[a]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[d]:			Adjusted Toxicity Value (ppb), as Dissolved[e], at Water Hardness:			Source
			m	h1	t1	x1	y1	15	50	286	15	50	286	
Freshwater Invertebrate	Cladoceran, *Daphnia magna*	Acute	1.72	50	1.1	3.9120	0.0953	0.14	1.1	22	0.14	1.1	22	Most acutely sensitive but chronic value is higher (i.e., ACR ≤1). Organisms are not fed during acute testing and this is considered one of the contributing factors for these ACRs. The second most acutely sensitive species was selected.
Freshwater Invertebrate	Mayfly, *Leptophlebia sp.* [g]	Acute	1.72	46.6	2.2	3.8416	0.7885	0.31	2.5	50	0.31	2.4	49	Brooke et al. 1986 as cited in USEPA 1987
Freshwater Invertebrate	Mayfly, *Leptophlebia sp.* [g]	Chronic	--	--	--	--	--	0.16	1.2	25	0.15	1.2	24	Estimated using ACR of 2 based on another sensitive invertebrate species, *Hyallela azeteca* (see Appendix C)
Freshwater Fish and Amphibians	Fathead minnow, *Pimephales*	Acute	1.72	75	5.0	4.3175	1.6094	0.31	2.5	50	0.31	2.4	49	Lemke 1981 as cited in USEPA 1987, 1980
Freshwater Fish and Amphibians	Fathead minnow, *Pimephales*	Chronic	--	--	--	--	--	0.015	0.12	2.3	0.014	0.11	2.3	Estimated using FACR of 21.39 (ACR of 15.70 from USEPA 1987 adjusted for use of NOEC rather than MATC).
5th Percentile Aquatic Animals	AWQC CMC[h]	Acute	1.72	50	1.1	3.9120	0.1387	0.14	1.15	23	0.12	0.98	20	Hardness-based National Recommended WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm
5th Percentile Aquatic Animals	AWQC CCC	Chronic	There is currently no chronic freshwater AWQC for silver.											Hardness-based National Recommended WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

[a]The acute slope of 1.72 is from Appendix B of current Recommended National Ambient WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

[b]Natural log values of water hardness (x = Ln(hardness)) at 15, 76, 136, and 286 mg $CaCO_3$/L are 2.7080, 3.9120, 4.3307, 4.9126, and 5.6560, respectively.

[c]Adjusted toxicity value (y) = m(x - x1) + y1 from point-slope linear relationship; see table footnote (b) for definition of x.

[d]Exp(y); see table footnote (b) for definition of y.

[e]Total recoverable values adjusted to dissolved using the conversion factor of 0.85 from Appendix B of current Recommended National Ambient WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm.

[f]Species mean acute value from results in USEPA 1987 adjusted to hardness of 50 mg/L as $CaCO_3$, and excluding value from Elnabarawy et al. 1986. Results from the hard water used in this laboratory for this species and others in the USEPA 1987 appear to be more toxic than similar hard water, and values tend to be greater than a factor of 10 from other adjusted values.

[g]The cladoceran acute values tended to be lower than chronic NOEC values (USEPA 1980, 1987). This is attributed to potentially mitigating effects of food for these as they are not fed in acute tests but are in the life-cycle tests. Therefore the next most acutely sensitive non-cladoceran species was identified and a chronic value estimated using an ACR of 2.

[h]The current CMC from Appendix B of current Recommended National Ambient WQC given as exp(1.72*[ln(hardness)-6.59], based on USEPA 1980. http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

Table 17 Effect Endpoints Selected for Assessing Risks from Silver to Saltwater Animals

Receptor Group	Representative Species[a,b]	Endpoint				Source
		Risk Scenario	Type	Toxicity Value, Total Recoverable (ppb)	Toxicity Value, Dissolved[c] (ppb)	
Saltwater fish	Summer flounder, *Paralichthys dentatus*	Acute	96-h LC_{50}	4.7	4.0	Cardin 1986 as cited in USEPA 1987, Eisler 1996, Howe and Dobson 2002
		Chronic	NOAEC	0.22	0.19	Estimated using ACR of 21.39 for pooled ACRs adjusted for use of NOEC versus MATC (see Table X)
Saltwater crustacean	Copepod, *Arcatia clausi*	Acute	96-h LC_{50}	13.3	11.3	Lussier and Cardin 1985 as cited in USEPA 1987
		Chronic	NOAEC	0.62	0.53	Estimated using ACR of 21.39 for pooled ACRs adjusted for use of NOEC versus MATC (see Table X)
Mollusk	American oyster (embryo-larva), *Crassostrea virginica*	Acute	IC_{50}	3.0	2.6	Zaroogian, manuscript as cited in USEPA 1987
5th Percentile Aquatic Animals	Species Distribution: AWQC CMC[b]	Acute	FAV/2	1.9	1.6	National Recommended WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm
	Species Distribution: AWQC CCC[b]	Chronic	MATC	--	--	

[a]The most acutely sensitive fish, crustacean, and mollusk species were select for representing a taxonomic group. If the species did not have a chronic NOEC value, one was estimated using an acute-to-chronic (ACR) approach.

[b]National ambient water quality criteria can potentially provide a more refined assessment. The final acute value (FAV) used to calculate the criterion maximum concentration (CMC) or acute criterion, and the criterion continuous concentration (CCC) or chronic value are provided.

[c]The study values are in terms of total recoverable metal. Recommended National Ambient Water Quality Criteria for this metal are in terms of dissolved metal, and the exposure concentrations from the MAMPEC model used in this assessment are also in terms of dissolved metal. Total recoverable zinc acute and chronic values are multiplied by 0.946 to convert them to dissolved zinc. The conversion factor is from the Appendix A dissolved conversion factor table for metals in the 2014 Recommended National Ambient Water Quality Criteria site http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm.

Table 18 Effect Endpoints Selected for Assessing Risks from Zinc to Freshwater Animals

Receptor Group	Representative Species	Risk Scenario	AWQC Pooled Slope[a]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[b,c,d]:			Adjusted Toxicity Value (ppb), as Dissolved[e], at Water Hardness:			Source
			m	h1	t1	x1	y1	15	50	286	15	50	286	
Freshwater Invertebrate	Cladoceran, *Ceriodaphnia reticulata*	Acute	0.8473	45	32	3.8067	3.4657	12.6	35.0	153.3	12.3	34.2	150	Carlson and Roush 1985 as cited in USEPA 1987
		Chronic	0.8473	50	11.7	3.9120	2.4596	4.2	11.7	51.3	4.2	11.5	50.6	Estimated using FACR of 2.984 (ACR of 1.994 from USEPA 1995 adjusted for use of NOEC rather than MATC), applied to the normalized (hardness 50 mg/L as $CaCO_3$) acute value and the pooled chronic slope.
Freshwater Fish and Amphibians	Striped bass, *Morone saxatilis*	Acute	0.8473	285	430	5.6525	6.0638	35.5	98.4	431	34.7	96.2	422	Palawski et al. 1985 as cited in USEPA 1987
		Chronic	0.8473	50	33	3.9120	3.4965	11.9	33.0	145	11.7	32.5	143	Estimated using FACR of 2.984 (ACR of 1.994 from USEPA 1995 adjusted for use of NOEC rather than MATC), applied to the normalized (hardness 50 mg/L as $CaCO_3$) acute value and the pooled chronic slope.
5th Percentile Aquatic Animals	AWQC CMC[f]	Acute	0.8473	100	120	4.6052	4.7860	24.0	67	292	23.5	65	285	Hardness-based National Recommended WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm
	AWQC CCC[g]	Chronic	0.8473	100	120	4.6052	4.7860	24.0	67	292	23.7	66	288	

[a]The acute and chronic slopes are from Appendix B of N

[b]Natural log values of water hardness (x = Ln(hardness)) at 15, 76, 136, and 286 mg $CaCO_3$/L are 2.7080, 3.9120, 4.3307, 4.9126, and 5.6560, respectively.

[c]Adjusted toxicity value (y) = m(x - x1) + y1 from point-slope linear relationship; see table footnote (b) for definition of x.

[d]Exp(y); see table footnote (b) for definition of y.

[f]The Final Acute Value in USEPA 1995 uses all the acute data in the USEPA 1987 Zinc AWQC document and two additional acute studies identified in the 1995 update. The hardness-based CMC from Appendix B of current Recommended National Ambient WQC given as exp(0.8473*[ln(hardness)-0.884]. The hardness-based CCC is the same as the CMC.

Table 19 Effect Endpoints Selected for Assessing Risks from Zinc to Saltwater Animals

Receptor Group	Representative Species[a,b]	Endpoint				Source
		Risk Scenario	Type	Toxicity Value, Total Recoverable (ppb)	Toxicity Value, Dissolved[c] (ppb)	
Saltwater fish	Cabezon, *Scorpaenichthys marmoratus*	Acute	96-h LC_{50}	191	181	Dinnel et al. 1983 as cited in USEPA 1987
		Chronic	NOAEC	46.0	43.5	Estimated using ACR of 4.158 for saltwater species from USEPA 1987 adjusted for use of NOEC rather than MATC (ACR has remained unchanged in subsequent updates to Zn)
Saltwater crustacean	Lobster (larva), *Homarus americanus*	Acute	96-h LC_{50}	175	166	Johnson 1985 as cited in USEPA 1987
		Chronic	NOAEC	42.1	39.8	Estimated using ACR of 4.158 for saltwater species from USEPA 1987 adjusted for use of NOEC rather than MATC (ACR has remained unchanged in subsequent updates to Zn)
Mollusk	Quahog clam (embryo), *Mercenaria mercenaria*	Acute	IC_{50}	195	184	Calabrese and Nelson 1974 as cited in USEPA 1987
5th Percentile Aquatic Animals	Species Distribution: AWQC CMC[b]	Acute	FAV/2	90	85	National Recommended WQC http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm
	Species Distribution: AWQC CCC[b]	Chronic	MATC	81	77	

[a]The most acutely sensitive fish, crustacean, and mollusk species were select for representing a taxonomic group. If the species did not have a chronic NOEC value, one was estimated using an acute-to-chronic (ACR) approach.

[b]National ambient water quality criteria can potentially provide a more refined assessment. The final acute value (FAV) used to calculate the criterion maximum concentration (CMC) or acute criterion, and the criterion continuous concentration (CCC) or chronic value are provided.

[c]The study values are in terms of total recoverable metal. Recommended National Ambient Water Quality Criteria for this metal are in terms of dissolved metal, and the exposure concentrations from the MAMPEC model used in this assessment are also in terms of dissolved metal. Total recoverable zinc acute and chronic values are multiplied by 0.946 to convert them to dissolved z inc. The conversion factor is from the Appendix A dissolved conversion factor table for metals in the 2014 Recommended National Ambient Water Quality Criteria site http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm .

Table 20 Aquatic organism RQs for freshwater inland marina scenarios from leached copper

Receptor Group	Risk Scenario	Copper (ppb) dissolved				RQs Small FW Marina		RQs Large FW Marina	
		Toxicity Endpoints		EECs					
		Softwater	Hardwater	FW Small Marina	FW Large Marina	Softwater	Hardwater	Softwater	Hardwater
Freshwater fish	Acute	1.62	26	60.2	182	**37**[a]	**2.3**[a]	**112**[a]	**7.0**[a]
	Chronic	0.59	7.3	37.3	124	**63**[b]	**5.1**[b]	**210**[b]	**17**[b]
Freshwater Invertebrate	Acute	3.31	53	60.2	182	**18**	**1.1**	**55**	**3.4**
	Chronic	1.21	15	37.3	124	**31**	**2.5**	**102**	**8.3**
AWQC CMC	Acute	2.25	36.2	60.2	182	***27***[c]	***1.7***	***81***	***5.0***
AWQC CCC	Chronic	1.77	22	37.3	124	***21***[c]	***1.7***	***70***	***5.6***
Aquatic Plants, Vascular	Nonlisted	1.2[f]	1.2[f]	37.8[f]	126[f]	**32**[d]	**32**[d]	**105**[d]	**105**[d]
	Listed	0.8[f]	0.8[f]	37.8[f]	126[f]	*47*[e]	*47*[e]	*158*[e]	*158*[e]
Aquatic Plants, Nonvascular	Nonlisted	119[f]	119[f]	37.8[f]	126[f]	<1	<1	**1.1**	**1.1**
	Listed	5.8[f]	5.8[f]	37.8[f]	126[f]	*6.5*	*6.5*	*22*	*22*

[a] Acute RQs: Values in bold and underlined exceed non-listed acute LOC of 0.5.

[b] Chronic RQs: Values in bold exceed the chronic LOC of 1.0.

[c] For AWQC CMC and CCC RQs: Values in bold and italicized exceed the CMC and CCC.

[d] Aquatic plant nonlisted RQs: Values in bold and underlined exceed the nonlisted aquatic plant LOC of 1.0.

[e] Aquatic plant listed RQs: Values in italic exceed the listed aquatic plant LOC of 1.0.

[f] Copper toxicity values and EECs are in terms of total.

Table 21 Aquatic organism RQs for saltwater marina and commercial harbor scenarios from leached copper

Receptor Group	Risk Scenario	Copper (ppb) dissolved			RQs	
		Toxicity Endpoints	EECs			
			Marina	Commercial Harbor	Marina	Commercial Harbor
Saltwater fish	Acute	9.88	113	32.4	**11.4**[a]	**3.3**[a]
	Chronic	3.2	78.2	11.5	**24.4**[b]	**3.6**[b]

Receptor Group	Risk Scenario	Copper (ppb) dissolved			RQs	
		Toxicity Endpoints	EECs			
			Marina	Commercial Harbor	Marina	Commercial Harbor
Saltwater crustacean	Acute	14.1	113	32.4	**8.0**	**2.3**
	Chronic	4.6	78.2	11.5	**17**	**2.5**
Saltwater mollusk	Acute	4.6	113	32.4	**25**	**7.0**
CMC	FAV/2	4.0	113	32.4	**28[c]**	**8.1**
CCC	Chronic	2.6	78.2	11.5	**30[c]**	**4.4**
Aquatic Plants, Nonvascular	Nonlisted	1.2[f]	79.3[f]	11.7[f]	**66[d]**	**9.8[d]**
	Listed	0.8[f]	79.3[f]	11.7[f]	*99[e]*	*15[e]*
Aquatic Plants, Vascular	Nonlisted	119[f]	79.3[f]	11.7[f]	<1	<1
	Listed	5.2[f]	79.3[f]	11.7[f]	*15*	*2.3*

[a]Acute RQs: Values in bold and underlined exceed non-listed acute LOC of 0.5.

[b] Chronic RQs: Values in bold exceed the chronic LOC of 1.0.

[c] For AWQC CMC and CCC RQs: Values in bold and italicized exceed the CMC and CCC.

[d] Aquatic plant nonlisted RQs: Values in bold and underlined exceed the nonlisted aquatic plant LOC of 1.0.

[e] Aquatic plant listed RQs: Values in italic exceed the listed aquatic plant LOC of 1.0.

[f] Copper toxicity values and EECs are in terms of total.

Table 22 Aquatic organism RQs for freshwater inland marina scenarios from leached silver

Receptor Group	Attribute Change	Silver (ppb) dissolved				RQs Small FW Marina		RQs Large FW Marina	
		Toxicity Endpoints		EECs					
		Softwater	Hardwater	FW Small Marina	FW Large Marina	Softwater	Hardwater	Softwater	Hardwater
Freshwater fish	Acute	0.31	49	1.3	4.0	**4.2[a]**	0.03	**13[a]**	*0.08[b]*
	Chronic	0.014	2.3	0.8	2.8	**57.1[c]**	<1	**200[c]**	**1.2[c]**
Freshwater Invertebrate	Acute[d]	0.14	22	1.3	4.0	**9.3**	*0.06*	**29**	*0.18*
	Acute[d]	0.31	49	1.3	4.0	**4.2**	0.03	**13**	*0.08*
	Chronic[d]	0.15	24	0.8	2.8	**5.3**	<1	**19**	<1

Receptor Group	Attribute Change	Silver (ppb) dissolved				RQs Small FW Marina		RQs Large FW Marina	
		Toxicity Endpoints		EECs					
		Softwater	Hardwater	FW Small Marina	FW Large Marina	Softwater	Hardwater	Softwater	Hardwater
AWQC CMC	Acute	0.12	20	1.3	4.00	**10.8**[e]	<1	**33**	<1
AWQC CCC	Chronic	none	none	0.8	2.8	--	--	--	--
Aquatic Plants, Nonvascular	Nonlisted	2.6[h]	2.6[h]	0.8[h]	2.8[h]	<1	<1	**1.1**[f]	**1.1**[f]
	Listed	1.2[h]	1.2[h]	0.8[h]	2.8[h]	<1	<1	*2.3*[g]	*2.3*[g]
Aquatic Plants, Vascular	Nonlisted	270[h]	270[h]	0.8[h]	2.8[h]	<1	<1	<1	<1
	Listed	No data	No data	0.8[h]	2.8[h]	NC	NC	NC	NC

NC: not calculated

[a]Acute RQs: Values in bold and underlined exceed the non-listed acute LOC of 0.5.

[b] Acute RQs: Values italicized and underlined exceed the listed acute LOC of 0.05.

[c] Chronic RQs: Values in bold exceed the chronic LOC of 1.0.

[d] Two species were selected for representing invertebrates. The first species a cladoceran was more sensitive than others, but chronic NOEC values were observed to be higher than acute EC_{50} values (ACRs <1.0) which is typically not acceptable. Acute tests for the species are conducted without feeding, whereas in chronic studies the animals are fed. The presence of food for these tests appears to ameliorate toxicity. The second acute value is for the second most acutely sensitive species, and the chronic value is for the same species (ACRs > 1.0).

[e] For AWQC CMC and CCC RQs: Values in bold and italicized exceed the CMC and CCC.

[f] Aquatic plant nonlisted RQs: Values in bold and underlined exceed the nonlisted aquatic plant LOC of 1.0.

[g] Aquatic plant listed RQs: Values in italics exceed the listed aquatic plant LOC of 1.0.

[h] Silver toxicity values and EECs are in terms of total.

Table 23 Aquatic organism RQs for saltwater marina and commercial harbor scenarios from leached silver

Receptor Group	Risk Scenario	Silver (ppb) dissolved			RQs	
		Toxicity Endpoints	EECs			
			Marina	Commercial Harbor	Marina	Commercial Harbor
Saltwater fish	Acute	4.0	2.5	0.69	**0.63**[a]	*0.17*[b]
	Chronic	0.19	1.7	0.25	**8.9**[c]	**1.3**[c]

Receptor Group	Risk Scenario	Silver (ppb) dissolved			RQs	
		Toxicity Endpoints	EECs			
			Marina	Commercial Harbor	Marina	Commercial Harbor
Saltwater crustacean	Acute	11.3	2.5	0.69	*0.22*	0.1
	Chronic	0.53	1.7	0.25	**3.2**	<1
Saltwater mollusk	Acute	2.6	2.5	0.69	**1.0**	0.27
CMC	FAV/2	1.6	2.5	0.25	**1.6[d]**	<1
CCC	Chronic	None	NA	NA	NA	NA
Aquatic Plants, Non-vascular	Nonlisted	2.6[g]	1.7[g]	0.25[g]	<1	<1
	Listed	1.2[g]	1.7[g]	0.25[g]	*1.4[f]*	<1
Aquatic Plants, Vascular	Nonlisted	270[g]	1.7[g]	0.25[g]	<1	<1
	Listed	No data	1.7[g]	0.25[g]	NC	NC

NA: not applicable; NC: not calculated

[a] Acute RQs: Values in bold and underlined exceed the non-listed acute LOC of 0.5.

[b] Acute RQs: Values italicized and underlined exceed the listed acute LOC of 0.05.

[c] Chronic RQs: Values in bold exceed the chronic LOC of 1.0.

[d] For AWQC CMC and CCC RQs: Values in bold and italicized exceed the CMC and CCC.

[e] Aquatic plant nonlisted RQs: Values in bold and underlined exceed the nonlisted aquatic plant LOC of 1.0.

[f] Aquatic plant listed RQs: Values in italics exceed the listed aquatic plant LOC of 1.0.

[g] Silver toxicity values and EECs are in terms of total.

Table 24 Aquatic organism RQs for freshwater inland marina scenarios from leached zinc

Receptor Group	Attribute Change	Zinc (ppb) dissolved				RQs Small FW Marina		RQs Large FW Marina	
		Toxicity Endpoints		EECs					
		Softwater	Hardwater	FW Small Marina	FW Large Marina	Softwater	Hardwater	Softwater	Hardwater
Freshwater fish	Acute	34.7	422	1.6	5.1	*0.05[a]*	<0.01	*0.15[a]*	0.01
	Chronic	11.7	143	1.0	3.5	<1	<1	<1	<1
Freshwater Invertebrate	Acute	12.3	150	1.6	5.1	*0.13*	0.01	*0.41*	0.03
	Chronic	4.2	50.6	1.0	3.5	<1	<1	<1	<1
AWQC CMC	Acute	23.5	285	1.6	5.1	<1	<1	<1	<1

Receptor Group	Attribute Change	Zinc (ppb) dissolved				RQs Small FW Marina		RQs Large FW Marina	
		Toxicity Endpoints		EECs					
		Softwater	Hardwater	FW Small Marina	FW Large Marina	Softwater	Hardwater	Softwater	Hardwater
AWQC CCC	Chronic	23.7	288	1.0	3.5	<1	<1	<1	<1
Aquatic Plants, Nonvascular	Nonlisted	19[b]	19[b]	1.0[b]	3.5[b]	<1	<1	<1	<1
	Listed	No data	No data	1.0[b]	3.5[b]	NC	NC	NC	NC
Aquatic Plants, Vascular	Nonlisted	10,000[b]	10,000[b]	1.0[b]	3.5[b]	<1	<1	<1	<1
	Listed	654[b]	654[b]	1.0[b]	3.5[b]	<1	<1	<1	<1

NC: not calculated

[a] Acute RQs: Values italicized and underlined exceed the listed acute LOC of 0.05.

[b] Zinc toxicity values and EECs are in terms of total.

Table 25 Aquatic organism RQs for saltwater marina and commercial harbor scenarios from leached zinc

Receptor Group	Risk Scenario	Zinc (ppb) dissolved			RQs	
		Toxicity Endpoints	EECs			
			Marina	Commercial Harbor	Marina	Commercial Harbor
Saltwater fish	Acute	181	3.1	0.87	0.02	<0.01
	Chronic	43.5	2.2	0.31	<1	<1
Saltwater crustacean	Acute	166	3.1	0.87	0.02	<0.01
	Chronic	39.8	2.2	0.31	<1	<1
Saltwater mollusk	Acute	184	2.2	0.87	0.01	<0.01
CMC	Acute	85	3.1	0.87	<1	<1
CCC	Chronic	77	2.2	0.31	<1	<1
Aquatic Plants, Nonvascular	Nonlisted	19[a]	2.2[a]	0.31[a]	<1	<1
	Listed	No data	2.2[a]	0.31[a]	NC	NC
Aquatic Plants, Vascular	Nonlisted	10,000[a]	2.2[a]	0.31[a]	<1	<1
	Listed	654[a]	2.2[a]	0.31[a]	<1	<1

[a] Zinc toxicity values and EECs are in terms of total.

3.3.1.3 Uncertainty

Proportion of Boats Treated with an Antifoulant

The model assumes that all boats would be treated with Tefcite. Alternatively this can also be viewed as all boats are treated with an antifoulant that has an equivalent leach rate for copper, silver, and zinc equivalent to that of Tefcite. Not all boats in marinas are likely to be treated with antifoulant but it is likely that a larger proportion of boats in saltwater are more likely to be treated than in freshwater due to differences in pest pressure between these environments, differences maintenance practices and use patterns of the boats. The proportion of boats in each type of environment that are likely treated with an antifoulant is unknown at this time. Information on this could help to refine estimates of risk.

Leaching Rates of Copper, Zinc, and Silver from Tefcite

RQs were calculated using EECs based on maximum leaching rate. This is the rate that would be expected for newly applied paint. Not all boats will have fresh antifoulant paint on their hulls or bottoms at the same time. Using the steady-state conditions an estimate of the impact to estimates of risk were conducted, details are provided in Appendix E. For silver not much of an impact on RQs are expected because the maximum and steady-state leach rates do not differ significantly. For zinc, because there were no exceedances of LOCs for the saltwater marina and commercial harbor or the fresh, hardwater conditions the steady-state has little impact except reducing exceedance for listed species. Exceedances for copper are still expected, an example for the saltwater marina and commercial harbor are provided in **Error! Reference source not found.**.

BLM and the Copper Stressor-Response Relationship

Risk estimates for evaluating potential adverse effects to freshwater aquatic animals were calculated using endpoints adjusted for water hardness alone. While this method accounts for some effects of water chemistry on toxicity of copper to aquatic animals, it can result in an overestimate of sensitivity and an over estimate of risk under some environmental conditions. The OW published copper criteria based on the BLM (USEPA 2007b) method in 2007, but the method requires parameterization of several water chemistry exposure conditions for application of the method. The freshwater inland marina scenarios currently being used by the agency do not have these values parameterized for a national assessment in the U.S. Therefore, RQs could not be calculated at this time using BLM adjusted effect endpoints. However, the degree to which using the BLM may have reduced risk estimates was evaluated; details of this evaluation are provided in Appendix F.

While use of the BLM method would have resulted in lower RQs for copper, the CMC would still be exceeded in both small and large freshwater marinas under a wide-range of water chemistry conditions.

3.3.2 Ecological Risk Description

The risk assessment conducted indicates there is potential for Tefcite applied to ship hulls and bottoms to exceed acute and chronic LOCs, and aquatic listed and non-listed LOCs due primarily to copper leaching from Tefcite in freshwater and saltwater marinas and from silver in marinas located in softwater environmental conditions.

Leaching of zinc was not indicated to result in exceedance of any LOC in the saltwater marina or commercial harbor scenarios or in freshwater, under hard water conditions. Zinc exceeded the acute listed species LOC in softwater marinas.

While under maximum leach rates for copper, acute and chronic LOCs were exceeded for copper, considering steady-state leach rate conditions reduces LOC exceedances to nonlisted vascular plants, and acute listed LOC for fish and invertebrates.

For copper the risk assessment considered not only maximum leach rates but also steady-state, and the impact of using copper toxicity values adjusted using the BLM rather than hardness-dependent approach. Copper from antifoulant paints has been identified as impairing waters in a number of freshwater and saltwater marinas. Three TMDLs have been found for copper in marinas.

The leach rates of copper from Tefcite in MRID 48772001 are lower than some other copper-containing aquatic paints. The maximum copper leach rate for Tefcite was 71 $\mu g/cm^2/day$ as compared to four other paints, with an average of 165 $\mu g/cm^2/day$ and a range of 97-208 $\mu g/cm^2/day$. Table 26 contains the individual rates. In addition, the agency also located a literature study (Finnie, 2006) which included "steady-state" leaching rates (21-45 day mean values) from ASTM studies on six different antifouling paints. In the Finnie (2006) study, the steady-state concentrations ranged from 48.6-131.2 $\mu g/cm^2/day$ with a mean rate of 82 $\mu g/cm^2/day$. Of the paints in the Finnie study, three of the six had steady state (21-45 day mean) leaching rates that were higher than the maximum rate for Tefcite. Based on the comparisons, Tefcite appears to have a lower emission rate than some other copper-containing antifoulant paints.

Table 26 Leach Rates of Copper from Other Antifoulant Paints Containing Copper

Paint (% Cuprous oxide)	Copper Leaching Rates (Maximum, units of $\mu g/cm^2/day$)	EPA Reg. No.	Reference (MRID)
American Chemet LoLo Tint 97 (48%)	195	26883-6	43760701
Nordox Cuprous Oxide Paint Grade (97 %)	208	48142-1	44175101
Aquaguard Plus (Red) Waterbase Antifouling Bottom Boat Paint (26.37 %)	97	9339-19	45687001
Flexguard XI Waterbase Preservative	160	Unknown	43339001
Average	**165**		

4 Summary

The use of Tefcite is not expected to result in human health risk of concern as long as the applicator wears the PPE which is required on the proposed label.

The use of Tefcite will be expected to result in potential risks of concern to aquatic animals and plants mainly from copper leaching from the paint. These risks are comparable to risks expected from other copper based antifoulant paints. EPA plans to conduct an ecological risk assessment for pesticidal uses of copper as part of the Registration Review of copper which will include a review of all copper based antifoulant paints. Registration Review may result in mitigation to address risks from copper in antifoulant paints.

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Appendix A: Environmental Fate Data

Use of Tefcite in Antifoulant Paint

Tefcite is a thermoplastic antifouling power coating to prevent hard and soft fouling on all boats and ships and can be used on the hulls and bottoms of pleasure and commercial vessels and stationary structures in fresh and salt water. It contains cuprous oxide (56.35 %), zinc (0.054 %), and silver (0.018 %). The metallic copper content is 50.045 %.[10] Because these metals are elements, they continue to cycle in the environment after release.

Copper Environmental Fate

This environmental fate assessment for copper is based on the Amended Copper RED.[11] Copper is a transition metal, with an atomic number of 29, an atomic weight of 63.5, and two naturally occurring isotopes. At a certain level, copper is an essential element for living systems, and is a key atom in the oxygen carrying protein, hemocyanin, for some invertebrates. Various forms of copper occur naturally in the environment. It is used in a wide variety of industrial and consumer applications, in addition to being used in pesticidal applications for over 100 years, thus in most areas where a copper containing pesticide is applied, it must be assumed that there is an existing background concentration that must be considered.

Copper occurs naturally in the environment, and is also introduced by a wide variety of anthropogenic sources, thus there is always a background concentration, and there is no way to distinguish the particular source. Studies, both in terrestrial and aquatic ecosystems, have shown that even in some cases where copper concentrations are elevated, toxic effects to organisms are not evident. This has been associated with the speciation[12] of copper, and the fact that Cu^{2+} will form inorganic and organic complexes, which may or may not be toxic. Additionally, Cu^{2+} has a high sorption affinity for soil, sediments, and organic matter which limits bioavailability. Because these factors are dependent on water chemistry as well as sediment/soil properties, the relative toxicity and bioavailability of Cu^{2+} is highly site specific.

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[10] Draft Label, Reintjes Marine Surfaces Techologies, LLC

[11] http://www.epa.gov/oppsrrd1/REDs/copper_red_amend.pdf

[12] Speciation is the relative proportion of total copper as cupric ion (Cu^{2+}), cuprous ion (Cu^{+}), inorganic complexes, organic complexes and minerals (amorphous or crystalline).

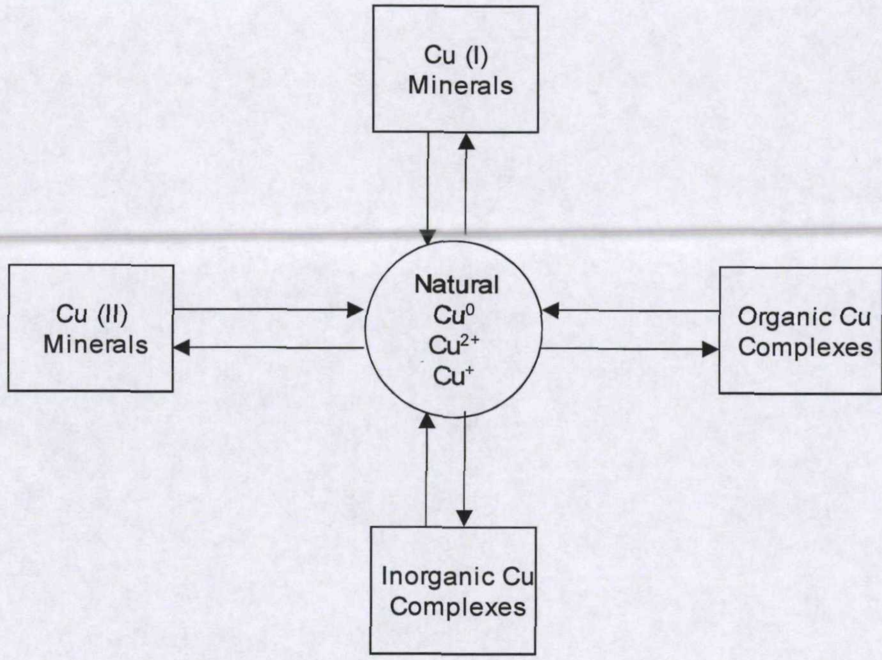

Figure 1– Environmental Fate Bridging Strategy for Cu Minerals and Complexe

Stability Constants for Cu Minerals

The construct of the stability diagrams assumes Cu^{2+} ion is the predominant ion due to oxic nature (pE+pH> 12) of surface water. These conditions were assumed because aquatic organisms require oxygen for normal biological function. Cupric (Cu^{2+}) ion activities in ambient surface waters suggest chemical equilibria conditions are not constant over a broad pH range (Figure 7). Copper activities in neutral and alkaline waters (pH>7) indicate supersaturation of cupric ferrite in equilibrium with soil Fe which exceeds the solubility of CuO (tenorite) under neutral and alkaline pH conditions. In acidic surface waters, however, Cu^{2+} activities appear to be in near equilibrium or undersaturated to soil Cu for both ambient and introduced Cu.

Environmental Fate of Zinc

Zinc is a naturally-occurring element with a divalent charge that is of relatively low abundance in nature (about 1 pound zinc in 1 million pounds of crust). As a mineral, it exists primarily as sphalerite [(ZnFe)S] in the earth's crust.[13] Zn reacts readily with non-oxidizing acids and releases hydrogen to produce divalent ions.[14] Depending on the halide complex, the water solubility can range from 1.57 mol/L for ZnF to 31.8 mol/L for $ZnCl_2$. The salts of the "oxo acids" such as nitrate, sulfate, sulfite, perchlorate, and acetate are soluble in water.[15] If Zinc is in a complex, the equilibrium constants range from 10^{-2} (for ZnI)

[13] Cotton and Wilkinson, p. 599
[14] Cotton and Wilkinson, p. 600
[15] Cotton and Wilkinson, p. 606

to 10^{21} for the CN^{1-} (cyanide) ion.[16] Based on these equilibrium constants, there would be one (1) free zinc in 100 ZnI molecules and virtually no free Zn with a Zn cyanide complex. In an aquatic environment intended for Tefcite use, the predominant Zn residue would be Zn^{2+} in fresh water and Zn(OH)2 in salt water because of the pH values of the different waters.[17]

Environmental Fate of Silver

Ambient Concentrations of Silver

Environmental sources of silver (Ag) are associated with natural mineral deposits and anthropogenic activities such as silver plating and antimicrobial uses. The total Ag concentration in soils can range from 0.01 to 5 mg/kg (Lindsay, 1979). Ambient concentrations of silver in surface water (open ocean) ranges between 0.024 to 0.56 ng/L and rivers and it varies between 0.01 to 140 ng/L away from point source discharges. (Ed: Anders W. Andren and Thomas W. Bober, 2002).

Environmental Chemistry of Ag^o

Silver shows multiple oxidation states. The valence or combining capacity of metallic Ag(0) is zero. Although there are three oxidation states of silver (Ag(I), Ag(II), Ag(III)), the predominate oxidation state of silver under normal environmental conditions is Ag(I).

Dissolved silver in soil solution or aquatic environments can exist as ionic silver (Ag(I)) and inorganic and organic complexes. The silver complexes control the concentration of Ag(I) in soil solution and aquatic environments. The chemical reactions, type of complexes, and stability constants of the inorganic silver minerals are known and established. Among the complexes, the iodide complex (AgI_2^-) is the most important inorganic complex controlling ionic silver concentrations in oxic (pe=8) soil solution or aquatic environments.

Another consideration is the importance of organic-silver complexes. A potential modeling approach addressing the incorporation of Ag(I) speciation is the Biotic Ligand Model (BLM) (http://yosemite.epa.gov/water/owrccatalog.nsf/0/e693bcf79893c3e085256e23005fcd3b?Open Document, *2009)*, which was used to address the importance of organic-metal complexes of copper (Cu(II)) .

Ionic silver (Ag(I)) in solution can precipitate to form crystalline minerals such as oxides, hydroxides, halides, sulfides, phosphates, molybates, carbonates, and nitrates. Equilibrium reactions, stability constants for Ag minerals are also well known and established. The Ag minerals can be important in controlling the Ag(I) concentration in soil solution or aquatic environments.

Sorption on sediment/soil surfaces through cation exchange processes is another process controlling environmental concentrations of Ag(I). Soil: water sorption coefficient for Ag range from 1.0 to 5.8 L/kg in soil, suspended sediment, and sediment (Allison and Allison, 2005).

[16] Cotton and Wilkinson, p. 608, Table 16-7
[17] Lindsay, p. 216

Appendix B. MAMPEC Inputs and Outputs used for Assessing Proposed Tefcite Use Pattern

Tefcite is intended to be used for mollusk control on the bottom and sides of treated boats and ships. Once the boats or ships are in the water, the metal oxide active ingredient or the metal cations are expected to leach continuously below the water line into the adjacent surface waters. To quantify emissions and estimate concentrations of these metals in surface water, sediment, and particulate matter to which aquatic life may be exposed, the agency used the marine antifoulant model and software package MAMPEC version 3.0 (v.3.0).[18] MAMPEC is an integrated hydrodynamic and chemical fate model which is used as a tool to predict the estimated concentrations for exposure assessment of antifoulants in marinas, harbors, rivers, estuaries and open waters. MAMPEC was originally developed by the Institute of Environmental Studies (Instituut voor Milieuvraagstukken, IVM), Free University (Vrije Universiteit, VU) of Amsterdam and Delft Hydraulics for the Antifoulant Working Group (AFWG) of the European Paint Makers Association (CEPE) in 1999, several updates have since been made.

The model provides prediction of environmental concentrations of antifouling products in six generalized "typical" marine environments (commercial harbor, estuarine harbor, marina, marina poorly flushed, open sea, and shipping lane). The model is also used for exposure assessment in freshwater systems and discharges of chemicals in ballast water. There are three types of inputs: 1) environmental parameters (hydrodynamics, water characteristics, etc. of the scenario); 2) emission parameters (sizes, numbers, surface area, leach rate, etc.); and 3) compound-specific inputs. Except for the leach rate and compound specific inputs, the agency has been using the standard OECD-EU scenarios (ESD-PT21) for environment and emission inputs for marine environments (van de Plassche and van deer Aa, 2004).

For the current modeling effort, the Agency conducted modeling for two freshwater marinas, including an inland marina (poorly-flushed) containing 75 boats and a Swiss marina (containing 299 boats. The saltwater environments modeled included a commercial harbor (136 boats) and the default marina (299 boats). MAMPEC does not include hardness as an input, and as a result, salinity was used as a surrogate for hardness in the fresh water scenarios. In fresh water, the salinity was modified to 0.035 parts-per-thousand (ppt) and the pH was adjusted to 7 (unitless). The leaching rates from treated paint in MRID 48772001 were used as inputs for the model, and the maximum leaching rate for copper (71.6 $\mu g/cm^2/day$) was 38X and 48X of the rates for zinc (1.9 $\mu g/cm^2/day$) and silver (1.5 $\mu g/cm^2/day$), respectively.

Table 27 contains the chemical and physical input properties for Cu, Zn, and Ag ions and Table 28 contains the scenario and emission inputs for the model, including the leaching rate which was used for boats that are at berth and moving. Table 29 and Table 30 contain the estimated environmental concentrations (EECs) of copper, zinc, and silver in water and sediment in a small, and large poorly-flushed freshwater marinas, respectively. Table 31 and Table 32 contain the EECs in a saltwater commercial harbor and the default saltwater marina scenarios, respectively. MAMPEC predictions among the metals for a given scenario were essentially proportional to leaching rate (MRID 48772001) ratios of the metals, with the copper:zinc ratio of 36-38X and a copper:silver ratio of 46-48X.

[18] http://www.deltares.nl/en/software/1039844/mampec/1232321

Table 27 Chemical-Specific and Leaching Rate Inputs for MAMPEC

MAMPEC 3 Model Inputs for Metals	Metal ion (unless stated)		
	Cu	Zn	Ag
Molecular mass (grams/mole)	63.5	65.4	107.87
Water Solubility at 20 °C (gram/cubic meter)	11[19]	9.5[20]	220[21]
K_d (cubic meter/kilogram)	**0.4 (sandy soil)** 3.6 (clay soil)[22]	0.0062-0.052 **(average of 0.027)**[23]	0.0021-0.0058 **(median is 0.0036)**[24]
Leaching Rates (µg/cm2/day)	**71.6**	1.9	1.5

Table 28 MAMPEC Scenario Inputs

Input	Scenario				Comments
	Inland Marina—Poorly Flushed	Swiss Marina	Commercial Harbor	Default Marina 400m Poorly Flushed	
Hydrodynamics					
Water type	Fresh	Fresh	Saltwater	Saltwater	Default
Tidal period (hour)	12.41	12.41	12.41	12.41	
Tidal difference (meter)	0	0	1.5	0	
Max distance density tide (kg/m^3)	0	0	0.4	0	
Non-tidal daily water level (meter)	0	0	0	0	
Flow velocity (F) meter/second	0.2	0.2	1	0.2	
Water characteristics					
SPM concentration (mg/l)	35	35	35	35	Default
POC concentration (mg/l)	1	1	1	1	
DOC concentration (mg/l)	2	2	2	2	
Chlorophyll (µg/l)	3	3	3	2	
Salinity (PSU)[25]	0.035	0.035	34	34	None
Temperature (°C)	15	15	15	15	Default
pH	7	7	8	8	Assumed

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19 Maximum non-mining background concentration in surface water of 1,098 ppb * 10 as a safety factor to account for environmental variability, ASTDR

20 Maximum background concentration in surface water of 950,000 ppb * 10 as a safety factor to account for environmental variability, ASTDR.

21 Solubility value of 22,000 ppb * 10 as a safety factor to account for environmental variability. ASTDR.

22 From EPA 2006 Assessment, Kd values of 400 and 3,600 L/kg divided by 1000 to obtain cubic meter/kg. Sandy soil value chosen based on ~21 % sand in ocean sediment (http://www.csun.edu/~aes15831/subjects/Oceanography/unit4/). Clay soil value not used because clay texture in ocean sediments is predominant only in abysmal areas where other textures are absent (http://www.centralia.edu/academics/earthscience/ocean/lectures/ocean_ch04_seds.pdf)

23 Singh et al., 2006, K_d Range of 6.2-52 L/kg, average of 27.2 L/kg (4 soils), divided by 1000 to obtain cubic meter/kg

24 U.S. EPA, July, 2005, Table 1, Kd values of 2.1-5.8 L/kg converted to M^3/kg

25 Salinity was used as a surrogate for hardness in the freshwater scenarios because the model does not contain an option to use hardness. Salinity was set to the percent of total dissolved anions and cations in softwater. The MAMPEC 3 model outputs were not sensitive to changes in salinity, so soft water was run in the model for soft water (15 mg/l hardness), hard water (286 mg/l hardness), and seawater (34 parts-per-thousand, ppt).

Input	Scenario								Comments
	Inland Marina—Poorly Flushed		Swiss Marina		Commercial Harbor		Default Marina 400m Poorly Flushed		
Layout									
Length (meter)	100		400		1,000		400		Default
Width (meter)	100		400		1,000		400		
Depth (meter)	3.5		3.5		15		3.5		
Mouth width (meter)	0		0		2,500		50		
General									
Latitude (° Northern Hemisphere)	50		50		50		50		Default
Sediment									
Depth mixed sediment (meter)	0.1		0.1		0.2		0.1		Default
Sediment density (kg/m^3)	1,000		1,000		1,000		1,000		
Degradation organic matter (1/day)	0		0		0		0		
Nett sedimentation velocity (meters/day)	1		1		1		1		
Fraction organic carbon in sediment (% as decimal)	0.02852		0.02852		0.02852		0.02857		
Emission									
Ship sizes (meter)	At berth	Moving	At berth	Moving	At berth	Moving	At berth	Moving	Default
0-10	0	0	0	0	0	0	0	0	
10-50	75	0	299	0	0	0	299	0	
50-100	0	0	0	0	57	8.75	0	0	
100-150	0	0	0	0	25.5	2.15	0	0	
150-200	0	0	0	0	24.5	2.05	0	0	
200-250	0	0	0	0	5.5	0.5	0	0	
250-300	0	0	0	0	7.5	0.6	0	0	
300-350	0	0	0	0	1.5	0.1	0	0	

Table 29 Estimated Environmental Concentrations of Copper, Zinc, and Silver in a Small, Freshwater Inland Marina Containing Soft Water and 75 Boats.

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Copper (maximum leaching rate in µg/cm^2/day)	**Maximum concentration**	61.1	60.2	24.1	2.9
	95 % concentration	61.1	60.2	24.1	2.9
	Average concentration	37.8	37.3	14.9	1.8
	Median concentration	37.8	37.3	14.9	1.8
	Minimum concentration	13.0	12.8	5.1	0.61
Zinc (maximum leaching rate in µg/cm^2/day)	**Maximum concentration**	1.6	1.6	0.044	0.0053
	95 % concentration	1.6	1.6	0.044	0.0053
	Average concentration	1.0	1.0	0.027	0.0032
	Median concentration	1.0	1.0	0.027	0.0032

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
	Minimum concentration	0.35	0.35	0.0093	0.0011
Silver (maximum leaching rate in µg/cm^2/day)	**Maximum concentration**	1.3	1.3	0.0046	0.00055
	95 % concentration	1.3	1.3	0.0046	0.00055
	Average concentration	0.80	0.80	0.0029	0.00034
	Median concentration	0.80	0.80	0.0029	0.00034
	Minimum concentration	0.27	0.27	0.00098	0.00012

Table 30 Estimated Environmental Concentrations of Copper, Zinc, and Silver in a Large Freshwater Inland Marina Containing Soft Water and 299 Boats.

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Copper (maximum leaching rate in µg/cm^2/day)	**Maximum concentration**	184	182	72.7	8.7
	95 % concentration	184	182	72.7	8.7
	Average concentration	126	124	49.8	6.0
	Median concentration	126	124	49.7	6.0
	Minimum concentration	62.8	61.9	24.8	3.0
Zinc (maximum leaching rate in µg/cm^2/day)	**Maximum concentration**	5.1	5.1	0.14	0.017
	95 % concentration	5.1	5.1	0.14	0.017
	Average concentration	3.5	3.5	0.095	0.11
	Median concentration	3.5	3.5	0.095	0.011
	Minimum concentration	1.8	1.8	0.048	0.0057
Silver (maximum leaching rate in µg/cm^2/day)	**Maximum concentration**	4.0	4.0	0.015	0.0017
	95 % concentration	4.0	4.0	0.015	0.0017
	Average concentration	2.8	2.8	0.010	0.0012
	Median concentration	2.8	2.8	0.010	0.0012
	Minimum concentration	1.4	1.4	0.0050	0.00060

Table 31 Estimated Environmental Concentrations of Copper, Zinc, and Silver in a Saltwater Commercial Harbor.

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Copper (maximum leaching rate in µg/cm²/day)	Maximum concentration	32.8	32.4	0.80	1.6
	95 % concentration	32.2	31.7	0.79	1.5
	Average concentration	11.7	11.5	0.29	0.56
	Median concentration	3.8	3.7	0.092	0.18
	Minimum concentration	0.46	0.45	0.011	0.022
Zinc (maximum leaching rate in µg/cm²/day)	Maximum concentration	0.88	0.87	0.024	0.0015
	95 % concentration	0.86	0.86	0.023	0.0014
	Average concentration	0.31	0.31	0.0084	0.00052
	Median concentration	0.10	0.10	0.0027	0.00017
	Minimum concentration	0.012	0.012	0.00033	0.000020
Silver (maximum leaching rate in µg/cm²/day)	Maximum concentration	0.69	0.69	0.0025	0.00015
	95 % concentration	0.67	0.67	0.0024	0.00015
	Average concentration	0.25	0.25	0.00089	0.000055
	Median concentration	0.079	0.079	0.00028	0.000018
	Minimum concentration	0.0095	0.0095	0.000034	0.0000021

Table 32 Estimated Environmental Concentrations of Copper, Zinc, and Silver in a Saltwater Default Marina.

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Copper (maximum leaching rate in µg/cm²/day)	Maximum concentration	115	113	45.2	5.4
	95 % concentration	115	113	45.2	5.4
	Average concentration	79.3	78.2	31.3	3.8
	Median concentration	79.2	78.1	31.2	3.8
	Minimum concentration	39.0	38.0	15.2	1.8

Compound		Total concentration (µg/l)	Dissolved (µg/l)	Suspended solid (µg/g dry weight)	Sediment after one year (µg/g) dry weight
Zinc (maximum leaching rate in µg/cm²/day)	**Maximum concentration**	3.1	3.1	0.084	0.010
	95 % concentration	3.1	3.1	0.081	0.010
	Average concentration	2.2	2.2	0.059	0.0070
	Median concentration	2.2	2.2	0.059	0.0070
	Minimum concentration	1.1	1.1	0.029	0.0034
Silver (maximum leaching rate in µg/cm²/day)	**Maximum concentration**	2.5	2.5	0.0089	0.0011
	95 % concentration	2.5	2.5	0.0089	0.0011
	Average concentration	1.7	1.7	0.0062	0.00074
	Median concentration	1.7	1.7	0.0062	0.00074
	Minimum concentration	0.84	0.84	0.0030	0.00036

Appendix C. Summary of Ecotoxicity Data for Copper, Zinc and Silver

The copper, zinc, and silver in the antifoulant paint consist of inorganic forms. Upon leaching these metals are not expected either in the water column or in sediment to form organometallic compounds of special dietary exposure concern. Based on fate characterization of the metals leaching from the antifoulant paint and potential exposure pathways, metal effects data for aquatic organisms in the water column and sediment are needed to assess risk to aquatic organisms. All three of the metals have national recommended water quality criteria[26] and chemical-specific criteria development documents (USEPA 1980, 1985, 1987, 1995, 2007b). Toxicity of metals in sediment to aquatic organisms is based on information in USEPA's (2005) procedures for the derivation of equilibrium partitioning sediment benchmarks for metals. Standards used to evaluate the acceptability of acute and chronic studies, including open literature, for use in development of ambient water quality criteria are essentially equivalent to those used by OCSPP in evaluating studies for use in ecological risk assessments[27], therefore all studies listed as useable within the criteria development documents are considered acceptable for use in this risk assessment.

The agency has started to include freshwater scenarios in assessing risks from antifoulant paints, most previous assessment of antifoulants have evaluated risks to only saltwater organisms. The need to assess freshwater exposure arises because there is currently no way v-ia label language to preclude a boat which has been treated with an antifoulant to enter fresh water. In freshwater there are a number of water chemistry factors that influence toxicity of metals to aquatic organisms. In evaluating potential risks to freshwater organisms, the effect of these factors were considered in selecting endpoints for the assessment.

Ecotoxicity Data for Copper

Terrestrial Animals

Copper (I) oxide acute oral data is used for both hazard labeling and assessment of acute risks to birds and as a surrogate for terrestrial-phase amphibians. One acute oral study with copper (I) oxide was submitted and classified as acceptable (MRID 42714501). The LD_{50} for copper (I) oxide is >2250 mg a.i./kg (or >982 mg Cu/kg) classifying the substance as practically non-toxic.

Species, Age or size	% Purity	Endpoints as Copper, total [as test substance]	Toxicity Category of Test Substance	Study Classification/ Source/ Comments
Mallard duck, *Anas platyrhynchos*, 25 weeks	Copper (I) oxide 98.3% (43.7% Cu)	14-d LD_{50} >982 mg Cu/kg [>2250 mg a.i./kg]	Practically non-toxic	Acceptable/ MRID 42714501

[26] http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

[27] http://www.epa.gov/pesticides/science/efed/policy_guidance/team_authors/endangered_species_reregistration_workgroup/esa_evaluation_open_literature.htm

Aquatic Animals

For this assessment the agency used data contained within USEPA ambient water quality criteria (AWQC) documents (USEPA 1985, 1995, 2007b). Until 2007 ambient water quality criteria (AWQC) for copper in freshwater were based on hardness-dependent models (USEPA 1995)[28]. This means that the acute and chronic toxicity endpoints for a given species decreases as water hardness decreases. For example, if the LC_{50} for *Ceriodaphnia reticulata* in hard water (e.g., 240 mg/L as $CaCO_3$) is 23 ppb under soft water conditions (e.g., 50 mg/L as $CaCO_3$) the LC_{50} would decrease to 5.2 ppb. In 2007, USEPA published a biotic ligand model (BLM) method for setting acute freshwater water quality criteria for copper (USEPA 2007b). As part of the 2007 update for copper AWQC, the Office of Water (OW) performed a comprehensive review of the publicly available open literature studies that evaluated effects of copper on freshwater aquatic organisms. Data from approximately 350 acute exposure studies were used to derive normalized LC_{50} values for freshwater organisms, including 15 species of invertebrates, 22 species of fish, and 1 amphibian species representing 27 different genera. Only acute toxicity data where the following test water chemistry parameters were known or could be estimated were included in the 2007 criteria development: alkalinity, dissolved organic carbon (DOC), pH, and the major anions (chloride and sulfate) and cations (calcium, magnesium, sodium, and potassium). Acute toxicity values were normalized to a reference exposure condition, which was selected for no specific scientific basis other than it is equivalent to conditions found in the agency's standard formulation recipe for a reconstituted moderately-hard water for use in aquatic testing (i.e., temperature = 20ºC, pH = 7.5, dissolved organic carbon (DOC) = 0.5 mg/L, calcium = 14.0 mg/L, magnesium = 12.1 mg/L, sodium = 26.3 mg/L, potassium = 2.1 mg/L, sulfate = 81.4 mg/L, chlorine = 1.90 mg/L, alkalinity = 65.0 mg/L and sulfur = 0.0003 mg/L). To convert the normalized values to different environmental conditions requires use of a computer equilibrium model (provided on-line by OW[29]) and inputs for temperature, pH, DOC, major geochemical cations (calcium, magnesium, sodium, and potassium), dissolved inorganic carbon (DIC, the sum of dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate), and other major geochemical anions (chloride, sulfate). Except for temperature, pH, and DOC, such factors are currently not included as inputs to the exposure model, MAMPEC v.3.0. While there are efforts to include such information in future versions of the MAMPEC model and freshwater scenarios used by the agency such an approach is not useable at this time. Therefore for this assessment the hardness-dependent method for deriving acute criteria from the previous copper criteria document (USEPA 1995) was used to derive effect endpoints for use in a soft and a hard water exposure scenario. Potential impact to risk estimates will discussed in the uncertainty subsection of the risk characterization section. Not all of the data included in the prior acute freshwater criteria development was included in 2007. This appears to be due primarily to the lack of water chemistry information on test water needed to incorporate the values into the BLM model. Data from approximately 235 acute exposure studies were used to derive normalized LC_{50} values (normalized to 50 mg/L $CaCO_3$) for freshwater organisms, including 27 species of invertebrates and 29 species of fish, representing 43 different genera. Excerpts from the USEPA 1985 and 1995 acute effects tables showing results for the more sensitive fish and invertebrate species adjusted to water hardness of 15, 50, and 236 mg/L are provided Table 33. The water hardness of 50 mg/L is the normalized condition and is provided for reference, the water hardness of 15 and 236 mg/L $CaCO_3$ reflect

[28] Criterion Maximum Concentration = exp(0.9422*[ln(hardness)-1.700]; Criterion Continuous Concentration = exp(0.08545*[ln(hardness)-1.702]

[29] http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/copper/2007_index.cfm

the soft and hard water scenarios, respectively, used in risk estimates in this assessment. The following discussion of sensitivity is in terms of total recoverable metal. Cladoceran species in the *Ceriodaphnia* and *Daphnia* genera are the more sensitive freshwater aquatic animals and the most sensitive invertebrate species. Values normalized to 50 mg/L $CaCO_3$ water hardness range from 5.2 µg/L for the cladoceran *Ceriodaphnia reticulata* to 10,241 µg/L for the stonefly, *Acroneuria lycorias*. There was a lower normalized value of 1.43 µg/L for *Daphnia magna* but this value was considered extreme as compared to other study values for this species. Under soft water conditions reflective of about a third of the nation the range is 1.69 µg/L for *C. reticulata* to 3,295 µg/L for *A. lycorias*. For freshwater fish the Northern squawfish, *Ptychochelius oregonensis*, had the lowest normalized species mean acute value (SMAV) of 16.67 µg/L as compared to the second most sensitive normalized SMAV of 38.89 µg/L for rainbow trout, *Oncorhynchus mykiss*. However, the lowest normalized test result was 10.7 µg/L for *O. mykiss*. The most sensitive acute freshwater invertebrate and fish studies were selected as endpoints for estimates of risk to freshwater animals, along with AWQC CMC and CCC values (Table 13).

Acceptable freshwater chronic toxicity data from early life stage tests, partial life-cycle tests, and full life-cycle tests were used from 29 tests including data for 6 invertebrate species and 10 fish species. In the 2007 criteria document, OW used an acute-to-chronic ratio (ACR) approach for determination of the AWQ criterion continuous concentration (CCC). The OW used a maximum allowable toxicant concentration (MATC), which is the geometric mean of the NOEC and LOEC, or a 20% inhibition concentration (IC_{20}) for determination of ACRs. The final ACR (FACR) used by the OW was 3.22 (USEPA 2007b). NOEC values are the standard chronic endpoints used in ecological risk assessments supporting antimicrobial registrations. Therefore the OW ACRs were adjusted to a NOEC basis (Table 34).

Acceptable acute studies were identified for 34 species of invertebrates and 18 species of fish in estuarine/marine environment (USEPA 1985, 1995). One acceptable chronic study was located for estuarine/marine (sheepshead minnow) and an estuarine/marine invertebrate (mysid shrimp) (USEPA 1995, 2007b). Acute values ranged from 5.3 µg/L for Pacific oyster, *Crassostrea gigas*, to 9,694 µg/L for Common rangia, *Rangia cuneata*. The most sensitive species were mollusks, Blue mussels, *Mytlius edulis*, and Pacific oysters, *C. gigas* with SMAVs of 5.8 and 7.81 µg/L, respectively. Summer flounder, *Paralichthys dentatus*, and the copepod, *Arcatia tonsa*, are the most sensitive saltwater fish and crustacean species. The most sensitive mollusk acute test, the most acutely sensitive fish and crustacean were selected for assessing risk to saltwater animal species. Estimates of chronic toxicity for the most acutely sensitive fish and crustacean species were made by applying the ACR of 3.05 discussed in the previous paragraph (Table 34).

Table 33 Excerpt of Acute Effects Data for the Most Sensitive Invertebrate and Fish Species from the USEPA 1985 and 1995 Copper Criteria Documents Showing Values Adjusted to Water Hardness of 15, 50, and 286 mg/L as $CaCO_3$

Test Information (Source)	Exposure Method	AWQC Pooled Slope[a]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[d]:			Adjusted Toxicity Value (ppb), as Dissolved[e], at Water Hardness:			SMAV$_{norm}$
		m	h1	t1	x1	y1	15	50	286	15	50	286	
Cladoceran, *Ceriodaphnia reticulata*	S, U	0.942	45	17	3.8067	2.8332	6.04	18.77	97	5.13	18.0	82	18.77
Cladoceran, *Daphnia magna*	S, U	0.942	-	12.7									NU
Cladoceran, *Daphnia magna*	S, U	0.942	226	200	5.4205	5.2983	15.54	48.3	250	13.20	46.36	212.2	
Cladoceran, *Daphnia magna*	S, U	0.942	45.3	9.8	3.8133	2.2824	3.46	10.8	56	2.94	10.32	47.3	
Cladoceran, *Daphnia magna*	S, U	0.942	99	85	4.5951	4.4427	14.37	44.66	231	12.213	42.9	196	
Cladoceran, *Daphnia magna*	S, U	0.942	99	50	4.5951	3.9120	8.45	26.27	136	7.184	25.2	115	
Cladoceran, *Daphnia magna*	S, M	0.942	52	26	3.9512	3.2581	8.06	25.1	130	6.85	24.1	110	
Cladoceran, *Daphnia magna*	S, M	0.942	105	30	4.6540	3.4012	4.80	14.91	77.1	4.078	14.32	65.5	
Cladoceran, *Daphnia magna*	S, M	0.942	106	38	4.6634	3.6376	6.02	18.7	97	5.12	18.0	82	21.18
Cladoceran, *Daphnia magna*	S, M	0.942	207	69	5.3327	4.2341	5.82	18.10	93.6	4.949	17.37	79.5	
Cladoceran, *Daphnia magna*	S, U	0.942	45	10	3.8067	2.3026	3.55	11.04	57	3.02	10.60	49	
Cladoceran, *Daphnia magna*	S, M	0.942	100	31.8	4.6052	3.4595	5.32	16.55	86	4.53	15.89	73	
Cladoceran, *Daphnia magna*	S, M	0.942	143	26	4.9628	3.2581	3.11	9.66	50	2.64	9.28	42	
Cladoceran, *Daphnia magna*	S, U	0.942	250	6.5	5.5215	1.8718	0.46	1.43	7	0.39	1.4	6	
Cladoceran, *Daphnia magna*	S, U	0.942	45	54	3.8067	3.9890	19.2	59.6	308.3	16.31	57.2	262	
Cladoceran, *Daphnia pulex*	S, U	0.942	45	10	3.8067	2.3026	3.55	11.0	57.1	3.02	10.6	49	25.42
Cladoceran, *Daphnia pulex*	S, U	0.942	45	53	3.8067	3.9703	18.8	58.5	303	16.0	56.2	257	
Cladoceran, *Daphnia pulicaria*	S, M	0.942	48	11.4	3.8712	2.4336	3.81	11.8	61.25	3.239	11.373	52.06	
Cladoceran, *Daphnia pulicaria*	S, M	0.942	48	9.06	3.8712	2.2039	3.03	9.41	49	2.57	9.0	41	
Cladoceran, *Daphnia pulicaria*	S, M	0.942	48	7.24	3.8712	1.9796	2.42	7.52	39	2.057	7.22	33.1	
Cladoceran, *Daphnia pulicaria*	S, M	0.942	44	10.8	3.7842	2.3795	3.92	12.18	63.0	3.331	11.69	53.5	9.263
Cladoceran, *Daphnia pulicaria*	S, M	0.942	45	9.3	3.8067	2.2300	3.30	10.27	53.1	2.808	9.9	45.1	
Cladoceran, *Daphnia pulicaria*	S, M	0.942	95	17.8	4.5539	2.8792	3.13	9.7	50	2.7	9.3	43	
Cladoceran, *Daphnia pulicaria*	S, M	0.942	145	23.7	4.9767	3.1655	2.80	8.7	45	2.4	8.3	38	

Test Information (Source)	Exposure Method	AWQC Pooled Slope[a]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[d]:			Adjusted Toxicity Value (ppb), as Dissolved[e], at Water Hardness:			$SMAV_{norm}$
		m	h1	t1	x1	y1	15	50	286	15	50	286	
Cladoceran, *Daphnia pulicaria*	S, M	0.942	245	27.3	5.5013	3.3069	1.97	6.1	32	1.7	5.9	27	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	30	19.9	3.4012	2.9907	10.4	32.2	166	8.80	30.9	141	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	32	22.4	3.4657	3.1091	11.0	34.1	176	9.33	32.7	150	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	31	28.9	3.4340	3.3638	14.6	45.3	234	12.4	43.5	199	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	31	30	3.4340	3.4012	15.1	47.1	243.3	12.9	45.2	206.8	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	30	30	3.4012	3.4012	15.6	48.5	251	13.3	46.6	213	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	101	176	4.6151	5.1705	29.2	90.8	469	24.8	87.1	399	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	101	40	4.6151	3.6889	6.64	20.6	107	5.64	19.8	90.6	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	99	33.1	4.5951	3.4995	5.59	17.4	89.9	4.76	16.7	76.4	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	102	30.7	4.6250	3.4243	5.05	15.7	81	4.29	15.1	69	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	101	46.3	4.6151	3.8351	7.7	23.9	123	6.5	22.9	105	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	99	47.9	4.5951	3.8691	8.1	25.2	130	6.9	24.2	110.6	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	100	48.1	4.6052	3.8733	8.1	25.0	129	6.8	24.0	110	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	100	81.1	4.6052	4.3957	13.6	42.2	218	11.5	40.5	185.5	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	98	85.9	4.5850	4.4532	14.66	45.6	236	12.46	43.7	200	42.50
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	370	232	5.9135	5.4467	11.33	35.2	182	9.63	33.8	154.73	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	366	70	5.9026	4.2485	3.5	10.7	55	2.93	10.3	47	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	371	82.2	5.9162	4.4092	4.00	12.4	64	3.40	11.9	55	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	361	298	5.8889	5.6971	14.89	46.3	239	12.66	44.4	203	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	169	5.2679	5.1299	15.16	47.1	244	12.88	45.2	207	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	85.3	5.2679	4.4462	7.65	23.8	123	6.50	22.8	105	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	83.3	5.2679	4.4224	7.47	23.2	120	6.35	22.3	102	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	103	5.2679	4.6347	9.24	28.7	148	7.85	27.6	126	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	274	5.2679	5.6131	24.58	76.4	395	20.89	73.3	336	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	128	5.2679	4.8520	11.48	35.7	185	9.76	34.3	157	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	221	5.2679	5.3982	19.82	61.6	319	16.85	59.2	271	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	165	5.2679	5.1059	14.80	46.0	238	12.58	44.2	202	

Test Information (Source)	Exposure Method	AWQC Pooled Slope[(a)]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[(d)]:			Adjusted Toxicity Value (ppb), as Dissolved[(e)], at Water Hardness:			SMAV$_{norm}$
		m	h1	t1	x1	y1	15	50	286	15	50	286	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	197	5.2679	5.2832	17.67	54.9	284	15.02	52.7	241	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	514	5.2679	6.2422	46.10	143	741	39.19	137.6	630	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	194	243	5.2679	5.4931	21.8	67.8	350	18.53	65.0	298	
Rainbow trout (alevin), *Salmo gairdneri*	FT, M	0.942	23	28	3.1355	3.3322	18.7	58.2	301	15.91	55.9	256	
Rainbow trout (swim-up), *Salmo gairdneri*	FT, M	0.942	23	17	3.1355	2.8332	11.4	35.3	183	9.66	33.9	155	
Rainbow trout (parr), *Salmo gairdneri*	FT, M	0.942	23	18	3.1355	2.8904	12.0	37.4	193	10.23	35.9	164	
Rainbow trout (smolt), *Salmo gairdneri*	FT, M	0.942	23	29	3.1355	3.3673	19.4	60.3	312	16.48	57.9	265	
Rainbow trout (adult), *Salmo gairdneri*	FT, M	0.942	42	57	3.7377	4.0431	21.6	67.2	347	18.37	64.5	295	
Rainbow trout (fry), *Salmo gairdneri*	FT, M	0.942	-	253									
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	125	200	4.8283	5.2983	27.1	84.4	436	23.1	81.0	371	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	125	190	4.8283	5.2470	25.8	80.1	414	21.9	76.9	352	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	125	210	4.8283	5.3471	28.5	88.6	458	24.2	85.0	389	
Rainbow trout, *Salmo gairdneri*	S, M	0.942	290	890	5.6699	6.7912	54.7	170	878	46.5	163	747	
Rainbow trout, *Salmo gairdneri*	-	0.942	90	190	4.4998	5.2470	35.1	109	565	29.9	105	480	
Rainbow trout, *Salmo gairdneri*	FT, M	0.942	120	80	4.7875	4.3820	11.3	35.1	181	9.59	33.7	154	
Northern squawfish, *Ptychochelius oregonensis*	FT, M	0.942	54	18	3.9890	2.8904	5.4	16.7	87	4.58	16.1	74	16.74
Excerpt from Table E-1 of USEPA 1995													
Cladoceran, Ceriodaphnia reticulata	S, U	0.942	240	23	5.4806	3.1355	1.69	5.2	27	1.43	5.0	23	
Cladoceran, Daphnia magna	S, U	0.942	240	41	5.4806	3.7136	3.01	9.4	48	2.56	9.0	41	
Cladoceran, Daphnia pulex	S, U	0.942	240	31	5.4806	3.4340	2.28	7.1	37	1.93	6.8	31	
Rainbow trout, Oncorhynchus mykiss	FT, M	0.942	9.2	2.8	2.2192	1.0296	4.44	14	71	3.8	13	61	

(a) Except for the final mean acute value in the first row, values are from Table 1 in USEPA 1985 adjusted to hardness of 50 mg/L as CaCO3 using, pooled slope of 0.942 from

USEPA 1985.

(b) Natural log values of water hardness (x = Ln(hardness)) at 15, 76, 136, and 286 mg CaCO3/L are 2.7080, 3.9120, 4.3307, 4.9126, and 5.6560, respectively.

I Adjusted toxicity value (y) = m(x – x1) + y1 from point-slope linear relationship; see table footnote (b) for definition of x.

(d) Exp(y); see table footnote I for definition of y.

(e) The current Final Acute Value from Appendix B of current Recommended National Ambient WQC given as exp(1.72*[ln(hardness)], based on USEPA 1980. http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

(f) Values from Elnabarawy et al. 1986 were excluded from SMAV calculations. Results from the hard water used in this laboratory for this species and others in the USEPA 1987 appear to be more toxic than hard water at other laboratories for the same species, and values tend to be greater than a factor of 10 from other adjusted values. These studies are shaded in orange.

Table 34 Copper AWQC ACRs Adjusted to NOEC Basis

Test Species	Hardness (mg/L as $CaCO_3$)	Acute value (ppb)	NOEC (ppb)	LOEC (ppb)	Chronic Value (ppb) = MATC[a]	Chronic IC_{20} (ppb)	ACR[b]	SMACR	ACR based on NOEC	SMACR Adjusted to NOEC	Reference/ Comments
Snail, *Campeloma decisum*	35-55	1673	8	14.8	10.88	8.73	191.64	171.19	–	–	Arthur & Leonard 1970 as cited in USEPA 1985, 1995, 2007b/ >factor 10 difference from other ACRs, not used in FACR
Snail, *Campeloma decisum*	35-55	1673	8	14.8	10.88	10.94	152.93		–	–	
Cladoceran, *Ceriodaphnia dubia*	179	28.42	6.3	9.9	7.90	–	3.60	2.85	4.51	2.60	Belanger et al. 1989 as cited in USEPA 2007b
Cladoceran, *Ceriodaphnia dubia*	94.1	63.33	<19.3	19.3	–	19.36	3.27		–		Belanger et al. 1989 as cited in USEPA 2007b
Cladoceran, *Ceriodaphnia dubia*	57	13.4	NR	NR	24.50	–	0.55		–		Oris et al. 1991 as cited in USEPA 2007b/ Value not used in SMACR because <1
Cladoceran, *Ceriodaphnia dubia*	-	17.974	12	32	19.60	9.17	1.96		1.50		Carlson et al. 1986 as cited in USEPA 2007b
Cladoceran, *Daphnia magna*	51	26	11.4	16.3	13.63	12.58	2.07	3.42	2.28	3.33	Chapman, et al. cited in USEPA 1985, 1995, 2007b
Cladoceran, *Daphnia magna*	104	33.76	20.0	43.0	29.33	19.89	1.70		1.69		
Cladoceran, *Daphnia magna*	211	69	7.2	12.6	9.53	6.06	11.39		9.58		
Cladoceran, *Daphnia pulex*	57.5	25.737	4.0	6.0	4.90	2.83	9.09	4.81	6.43	4.68	

Test Species	Hardness (mg/L as $CaCO_3$)	Acute value (ppb)	NOEC (ppb)	LOEC (ppb)	Chronic Value (ppb) = MATC[a]	Chronic IC_{20} (ppb)	ACR[b]	SMACR	ACR based on NOEC	SMACR Adjusted to NOEC	Reference/ Comments
Cladoceran, *Daphnia pulex*	115	27.6	5.0	10.0	7.07	–	3.90		5.52		Winner 1985 as cited in USEPA 2007b
Cladoceran, *Daphnia pulex*	230	28.79	10	15	12.25	9.16	3.14		2.88		
Rainbow trout, *Oncorhynchus mykiss*	120	80	–	–	–	27.77	2.88	2.88	–	–	Seim et al. 1984 as cited in USEPA 2007b
Chinook salmon, *Oncorhynchus tshawytscha*	20-45	33.1	<7.4	7.4	–	5.92	5.59	5.59	–	–	Chapman 1975, 1982 as cited in USEPA 2007b
Bluntnose minnow, *Pimephales notatus*	172-230	231.99	<18	18	–	18	12.89	12.89	NU	–	Horning and Neiheisel 1979 as cited in USEPA 2007b/ Not used in FACR calculation; ACR related to sensitivity, not sensitive species
Fathead minnow, *Pimephales promelas*	45	106.875	NR	NR	–	9.38	11.39	11.39	NU	–	Lind et al. 1978 as cited in USEPA 2007b/ Not used in FACR calculation; ACR related to sensitivity, not sensitive species
Bluegill, *Lepomis macrochirus*	21-40	1100	21	40	28.98	27.15	40.52	40.52	NU	–	Lind et al. 1978 as cited in USEPA 2007b/ Not used in FACR calculation; ACR related to sensitivity, not sensitive species
Sheepshead minnow, *Cyprinodon variegatus*	–	368	172	362	250	206.7	1.47	1.47	2.140	2.140	Hughes et al. 1989 as cited in USEPA 2007b
Final mean acute-to-chronic ration (FMACR) for freshwater								3.22		3.05	

[a] Maximum acute threshold concentration (MATC) which is the geometric mean of the NOEC and LOEC values. This value was historically used to calculate ACRs. In the USEPA 2007 update, in addition to ACRs listed based on the MATC, ACRs based on the chronic IC_{20} were calculated also and were used in place of the MATC for a number of studies in determination of the final acute-to-chronic ratio (FACR). For risk assessments with antimicrobials a specific ICp for use as a NOEC which would be a surrogate not just for the species tested but for the species being represented has not been determined.

[b] Chronic IC_{20} values were used in place of the MATC for calculating ACRs in the USEPA 2007 ambient water quality criteria document. Therefore where a definitive NOEC was not determined, an ACR was still able to be calculated in this case.

Aquatic Plants

Acceptable aquatic plant toxicity data useful to the risk assessment is available from studies submitted to the agency, and US AWQC documents (USEPA 1985, 2007b). Neither the hardness-dependent criteria nor the BLM method directly incorporates toxicity data on aquatic plant species into calculations of AWQC. As part of setting the AWQC criteria values based on toxicity to aquatic animals is compared to aquatic plant toxicity data to evaluate whether or not the criteria would also be protective of aquatic plants. This was the case determined for copper AWQC (USEPA 1985, 2007b,). Standard guideline studies submitted to OPP will be used to derive toxicity endpoints for aquatic plants. The most sensitive aquatic plant species tested, the green alga, *Pseudokirchneriella subcapitata*, (EC_{50} = 1.2 ppb copper, NOEC = 0.80 ppb copper) was selected to represent non-listed algal species. For the vascular plant receptor group the most sensitive aquatic vascular plant study which was the duckweed, *Lemna minor* with a 5-d EC_{50} = of 119 ppb copper. An estimated NOEC of 39.8 ppb copper was used in the assessment.

Table 35 Summary of Copper Toxicity to Aquatic Plants

Species, Age or size	% Purity	Design Exposure Type/ pH/ hardness/ temperature	Endpoints as Copper, total in ppb [as test substance in ppb]	Study Classification/ Source/ Comments
Freshwater Species				
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CSP 99.9% (39.8% Cu)	S/ 7.9/ / 24°C	5-d IC_{50} = 1.2 [3.1] NOEC = 0.80 [2.0] unmeasured	Acceptable/ MRID 43363603/
Bluegreen alga, *Anabaena flos-aquae*	CSP 99.9% (39.8% Cu)	S/ 7.5-8.0/ / 24°C	5-d IC_{50} = 12 [31] NOEC = 7.9 [20] unmeasured	Acceptable/ MRID 43363602
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	S/ / 16 /	4-d EC_{50} = 38 (cell density) unmeasured	Chen et al. 1997 as cited in USEPA 2007b
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	S/ / 9.3 /	4-d EC_{50} = 44.3 (cell count) unmeasured	Blaise et al. 1986 as cited in USEPA 2007b
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	S/ / 9.3 /	4-d EC_{50} = 48.4 (cell count) unmeasured	Blaise et al. 1986 as cited in USEPA 2007b
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	S/ / 9.3 /	4-d EC_{50} = 46.4 (cell count) unmeasured	Blaise et al. 1986 as cited in USEPA 2007b
Diatom, *Navicula pelliculosa*	CSP 99.9% (39.8% Cu)	S/ 7.5-8.0/ / 24-25°C	5-d IC_{50} = 49.7 [125] NOEC = 24.9 [62.5] unmeasured	Acceptable/ MRID 43363601
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	R/ / 24.2 /	4-d EC_{50} = 48.2 (cell count) unmeasured	Radetski et al 1995 as cited in USEPA 2007b
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	S/ / 24.2 /	4-d EC_{50} = 54.4 (cell count) unmeasured	Radetski et al 1995 as cited in USEPA 2007b
Green alga, *Chlorella vulgaris*	CS	F/	4-d EC_{50} = 62 (cell numbers) unmeasured	Ferard et al. 1983 as cited in USEPA 1985, 2007b

Species, Age or size	% Purity	Design Exposure Type/ pH/ hardness/ temperature	Endpoints as Copper, total in ppb [as test substance in ppb]	Study Classification/ Source/ Comments
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	S/ / 9.3 /	4-d EC_{50} = 65.7 (cell count) unmeasured	St. Laurent et al. 1992 as cited in USEPA 2007b
Green alga, *Pseudokirchneriella subcapitata*[(a)]	CS	S/ / 9.3 /	4-d EC_{50} = 69.6 (cell count) unmeasured	St. Laurent et al. 1992 as cited in USEPA 2007b
Green alga, *Chlorella vulgaris*	CS	S/	4-d IC_{50} = 270 dissolved measured	Ferard et al. 1983 as cited in USEPA 2007b
Green alga, *Chlorella vulgaris*	CC	S/	4-d EC_{50} = 200 (cell density) measured	Blaylock et al. 1985 as cited in USEPA 2007b
Green alga, Pseudokirchneriella subcapitata[(a)]	CS	S/ / 24.2/	4-d IC_{50} = 400 (cell count) measured	Blaylock et al. 1985 as cited in USEPA 2007b
Green alga, *Chlorella saccharophila*	CS	S/	4-d EC_{50} = 550 unmeasured	Rachiln, et al. 1982 as cited in USEPA 1985, 2007b
Green alga, *Chlamydomonas reinhardtii*	CS	S/ / 90 -133 /	72-h NOEC 12.2 - 43 (cell density) measured	Winner and Owen 1991 as cited in USEPA 2007b
Diatom, *Nitzschia linearis*			5-d EC_{50} = 795 - 815 unmeasured	Academy ot Natural Sciences, 1960; Patrick, et al. 1968 as cited in USEPA 1985, 2007b
Diatom, *Navicula incerta*	CC	S/	4-d EC_{50} = 10,450 unmeasured	Rachiln, et al. 1982 as cited in USEPA 1985, 2007b
Duckweed, Lemna minor		F/	7-d EC_{50} = 119 unmeasured	Walbridge 1977 as cited in USEPA 1985, 2007b
Duckweed, *Lemna minor*	CSP 99.9% (39.8% Cu)	S/ 5.2-5.4/ /24-25°C	5-d IC_{50} = 915 [2,300] NOEC = 39.8 [100] unmeasured	Supplemental/ MRID 43363604/
Estuarine/Marine Species				
Dinoflagellate, *Scrippsiella faeroense*			5-d EC_{50} = 5 (growth rate) unmeasured	Saifullah 1978 as cited in USEPA 1985
Marine diatom, *Skeletonema costatum*	CCD >99%	S	72-hr IC_{50} = 9.42 [9.52] unmeasured	Supplemental/ MRID 46996107/
Dinoflagellate, *Prorocentrum micans*			5-d EC_{50} = 10 (growth rate) unmeasured	Saifullah 1978 as cited in USEPA 1985
Marine diatom, Asterionella japonica			72-hr EC_{50} = 12.7 (growth rate)	Fisher and Jones 1981 as cited in USEPA 1985
Marine diatom, *Phaeodactylum tricornutum*	CCD >99%	S	72-hr IC_{50} = 14.6	Supplemental/ MRID 46996108/
Dinoflagellate, *Gymnodinium splendens*			5-d EC_{50} = 20 (growth rate) unmeasured	Saifullah 1978 as cited in USEPA 1985
Marine diatom, *Nitschia closterium*			4-d EC_{50} = 33 (growth rate) unmeasured	Rosko and Rachlin 1975 as cited in USEPA 1985

Species, Age or size	% Purity	Design Exposure Type/ pH/ hardness/ temperature	Endpoints as Copper, total in ppb [as test substance in ppb]	Study Classification/ Source/ Comments
Marine diatom, *Skeletonema costatum*	CSP 99.9% (39.8% Cu)	S/ 6.7-7.6/ / 24-25oC	5-d IC_{50} = 119 [300] NOEC = 48.7 [125] unmeasured	Acceptable/ MRID 43363605/
Macro algae, *Fucus vesiculosus*	CCD	F	14-d IC_{50} = 44,104 [44,500] unmeasured	Supplemental/ MRID 46996105/

CCC: copper chloride dihydrate; CSP: copper sulfate pentahydrate

S: static; F: flow-through; R: static-renewal

[a] Formerly *Selenastrum capricornutum*

Ecotoxicity Data for Silver

Terrestrial Animals

There is one acute oral study (MRID 46453301) on a high purity grade silver salt, silver chloride, in the inhouse database (Table 36). Silver chloride is classified as practically non-toxic (LD_{50}>2250 mg a.i./kg), expressed in terms of the amount of silver, the LD_{50} is >1,687 mg Ag/kg. An acute oral study with colloidal silver at a single dose showed no effects at 420 mg Ag/kg-bw (USEPA 1992).

Table 36 Silver Effects Data for Birds

% Purity	Endpoints as Silver, total [as test substance]	Toxicity Category of Test Substance	Study Classification/ Source/ Comments
Silver chloride 99.6% (75% Ag)	15-d LD_{50} >1687 mg Ag/kg [>2250 mg a.i./kg] 15-d NOAEL = 1012 mg Ag/kg [1350 mg a.i./kg]	Practically non-toxic	Acceptable/ MRID 46453301

Aquatic Animals

The agency used data contained within the USEPA AWQC silver documents (1980, 1987) for selecting endpoints. Data summarized in Eisler (1996) and Howe and Dobson (2002) were also considered, as in previous silver assessments. The following summarizes the data available in the 1987 AWQC public draft for silver (USEPA 1987). Acceptable data on acute effects of silver in freshwater was available for 12 species of invertebrates and 7 species of fish. Results in the 1987 public draft were not adjusted to a normalized hardness, whereas they were in the 1980 AWQC document. The public draft discusses issues associated with the hardness-dependent slope used to develop criteria in the 1980 AWQC, but the proposed silver criteria were not updated based on the 1987 approach. To be consistent with the current hardness-dependent criteria, with the exception of data from Goettl and Davies (1978), acute toxicity values were adjusted to a normalized hardness using the pooled slope of 1.72 from the 1980 AWQC document before selection of the most sensitive test and species. Hard water in Goettl and Davies (1978) tests was unusually toxic and therefore not used in setting the pooled slope. For selection of the most sensitive result for the risk assessment, results from Goettl and Davies (1978) were adjusted using the pooled slope of 0.341 from the three Goettl and Davies (1978) studies (0.098, 0.4815, 0.4444) to adjust their data for water hardness. There is also an additional public literature 96-hour LC_{50} of 1.9 ppb for the freshwater amphipod, *Hyallela azeteca,* (Howe and Dobson, 2002) which has been used in previous assessments of silver, because it was identified as the second most sensitive species as compared to cladocerans. Adjusting this value using the pooled slope of 1.72 (USEPA 1980) results in adjusted values of 0.41, 3.5, and 70 ppb silver, total at water hardness of 15, 50, and 286 mg/L, respectively. Excluding those values identified as outliers in the public draft, acute toxicity values normalized to a water hardness of 50 mg/L, ranged from 0.44 ppb for the cladoceran, *Daphnia magna*, to 3,402 ppb for the midge, *Tanytarsus dissimilis* (Table 37). There is chronic data for this species but all the ACRs are <1 (Table 38). These animals are not fed during acute testing but they are during chronic tests, and the presence of food appears to provide some protection from acute effects. This species was included in calculation of the silver AWQC and was therefore included in the risk assessment, but instead of using the lowest study value the normalized SMAV of 1.08 ppb was used and the second most sensitive invertebrate included to allow determination of a reasonable chronic value for a sensitive invertebrate species that was not higher than the acute. The second most sensitive invertebrate species is a mayfly, *Leptophlebia* sp., with a normalized 96-hour LC_{50} of 2.5 ppb (Table 37). The most sensitive freshwater fish test was with a fathead minnow, *Pimephales promelas*, with a normalized 96-hour LC_{50} of 2.5 ppb, the normalized fathead minnow SMAV is 9.5 ppb (Table 37). Two other fish species had lower normalized SMAVs, the speckled dace, *Rhinichthys osculus* (normalized SMAV = 6.8 ppb) and the mottled sculpin, *Cattus bairdi*, (normalized SMAV = 7.0 ppb), but no test result for these species were lower than that of the Fathead minnow (Table 37), therefore the Fathead minnow value was used in the assessment. To convert these values to dissolved metal the current national recommended conversion factor of 0.85 for silver acute studies was applied (Table 13 and Table 37).

For saltwater in the 1987 AWQC public draft, there are acute studies with ten species of invertebrates, including five molluscs, four crustaceans and a polychaete, and eleven species of fish. The acute values range from 3 ppb for the Eastern oyster, *Crassostrea virginica*, for an embryo-larval study to >1,000,000 ppb for the mummichog, a value in excess of silver's solubility. For a risk assessment of saltwater species a minimum of three tests with a mollusk, shrimp, and fish are used. Information for each of these was available in this data set and the most sensitive study for a mollusk, fish, and non-mollusk invertebrate (Eastern oyster, *C. virginica*; Summer flounder, *Paralichthys dentatus*; and the copepod, *Arcatia tons*a) was used in the assessment (Table 17).

Acceptable chronic toxicity data was available in the 1987 public draft, for a freshwater cladoceran, *D. magna*, two freshwater species of fish the Rainbow trout, *Oncorhynchus mykiss*, and the Fathead minnow *P. promelas,* and a saltwater invertebrate, the mysid *Americamysis bahia* (Table 38). Also considered in previous silver assessments is the chronic toxicity value for the freshwater amphipod *H. azteca* of 0.95 ppb (Howe and Dobson 2002). There is insufficient information for a chronic AWQC development and none currently exists. Therefore this risk assessment chronic toxicity values were estimated using an ACR approach. As indicated previously a valid ACR for cladocerans cannot be determined because the ACRs are <1 (Table 38). The ACR for *H. azteca,* a species of similar acute sensitivity as the cladoceran and mayfly is 2.0 (1.9/0.95 = 2). This differs by about a factor of 10 from the 1987 FACR adjusted to a NOEC basis of 21.39 (Table 38). Therefore for this risk assessment, the *H. azteca* ACR of 2.0 was used

Table 37 Excerpt of Acute Effects Data for the Most Sensitive Invertebrate and Fish Species from the USEPA 1987 Silver Criteria Documents Showing Values Adjusted to Water Hardness of 15, 50, and 286 mg/L as $CaCO_3$

Test Species	Exposure Method	AWQC Pooled Slope[a]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[d]:			Adjusted Toxicity Value (ppb), as Dissolved[e], at Water Hardness:			SMAV
		m	h1	t1	x1	y1	15	50	286	15	50	286	
AWQC CMC[f]	--	1.72	50	1.23	3.9120	0.2070	0.155	1.23	24.7	0.132	1.05	21.0	--
Cladoceran, *Daphnia magna*	S, M	1.72	54	2.2	3.9890	0.7885	0.24	1.9	39	0.21	1.6	33	1.08
Cladoceran, *Daphnia magna*	S, M	1.72		1.07									
Cladoceran, *Daphnia magna*	S, M	1.72		0.64									
Cladoceran, *Daphnia magna*	S, U	1.72		0.39									
Cladoceran, *Daphnia magna*	S, M	1.72	255	48	5.5413	3.8712	0.37	2.9	58	0.31	2.5	50	
Cladoceran, *Daphnia magna*	S, M	1.72	255	55	5.5413	4.0073	0.42	3.3	67	0.36	2.8	57	
Cladoceran, *Daphnia magna*	S, M	1.72	73	8.4	4.2905	2.1282	0.55	4.4	88	0.47	3.7	75	
Cladoceran, *Daphnia magna*	S, M	1.72	73	14.9	4.2905	2.7014	0.98	7.8	156	0.83	6.6	133	
Cladoceran, *Daphnia magna*	S, M	1.72	60	1.1	4.0943	0.0953	0.10	0.8	16	0.09	0.68	13.7	
Cladoceran, *Daphnia magna*	S, M	1.72	60	0.6	4.0943	-0.5108	0.06	0.4	9	0.05	0.37	7.5	
Cladoceran, *Daphnia magna*	S, M	1.72	46	0.63	3.8286	-0.4620	0.09	0.73	15	0.078	0.6	12	
Cladoceran, *Daphnia magna*	S, M	1.72	46	0.66	3.8286	-0.4155	0.10	0.76	15	0.082	0.6	13	
Cladoceran, *Daphnia magna*	S, M	1.72	46	0.9	3.8286	-0.1054	0.13	1.0	21	0.11	0.9	18	
Cladoceran, *Daphnia magna*	S, M	1.72	46	1.03	3.8286	0.0296	0.15	1.19	23.9	0.127	1.01	20.3	
Cladoceran, *Daphnia magna*	S, M	1.72	54	2.9	3.9890	1.0647	0.32	2.5	51	0.27	2.2	43	
Cladoceran, *Daphnia magna*	S, M	1.72	47	0.24	3.8501	-1.4271	0.03	0.27	5.4	0.029	0.23	4.6	
Cladoceran, *Daphnia magna*	S, M	1.72	60	1.1	4.0943	0.0953	0.10	0.80	16	0.09	0.68	14	
Cladoceran, *Daphnia magna*	S, M	1.72	39	0.6	3.6636	-0.5108	0.12	0.92	18	0.10	0.78	16	
Cladoceran, *Daphnia magna*	S, U	1.72	72	1.5	4.2767	0.4055	0.10	0.80	16	0.09	0.68	14	
Cladoceran, *Daphnia magna*	S, U	1.72	240	10	5.4806	2.3026	0.08	0.67	14	0.07	0.6	11	
Cladoceran, *Daphnia magna*	S, U	1.72	240	1.5	5.4806	0.4055	0.01	0.10	2.0	0.01	0.1	2	[f]
Cladoceran, *Daphnia magna*	F, M	1.72	44.7	0.9	3.8000	-0.1054	0.14	1.1	21.9	0.12	0.9	19	
Cladoceran, *Daphnia pulex*	S, U	1.72	45	14	3.8067	2.6391	2.12	17	337	1.8	14.3	286	
Cladoceran, *Daphnia pulex*	S, U	1.72	240	1.9	5.4806	0.6419	0.016	0.1	2.57	0.014	0.109	2.18	[f]
Mayfly, *Leptophlabia* sp.	S, M	1.72	46.6	2.2	3.8416	0.7885	0.313	2.48	49.9	0.266	2.111	42.4	2.48
Fathead minnow, *Pimephales promelas*	S, M	1.72	48	30.43	3.8712	3.4154	4.115	32.6	655	3.50	27.7	557	9.5
Fathead minnow, *Pimephales promelas*	S, M	1.72	255	230	5.5413	5.4381	1.759	14.0	280	1.50	11.9	238	
Fathead minnow, *Pimephales promelas*	S, M	1.72	54	13.8	3.9890	2.6247	1.524	12.1	243	1.30	10.3	206	
Fathead minnow, *Pimephales promelas*	S, M	1.72	46.1	6.7	3.8308	1.9021	0.971	7.7	155	0.826	6.55	131	
Fathead minnow, *Pimephales promelas*	S, M	1.72	75	10.3	4.3175	2.3321	0.647	5.1	103	0.550	4.36	87.5	
Fathead minnow, *Pimephales promelas*	S, M	1.72	48	22.66	3.8712	3.1206	3.06	24	488	2.60	20.7	415	
Fathead minnow, *Pimephales promelas*	S, M	1.72	255	270	5.5413	5.5984	2.07	16.4	329	1.76	13.9	280	
Fathead minnow, *Pimephales promelas*	S, M	1.72	54	19.6	3.9890	2.9755	2.16	17	345	1.84	14.6	293	
Fathead minnow, *Pimephales promelas*	S, M	1.72	46.1	12.3	3.8308	2.5096	1.78	14.1	284	1.52	12.0	241	

Test Species	Exposure Method	AWQC Pooled Slope[a]	Actual Study Hardness	Study Toxicity Value (ppb)	Ln(h1)	Ln(t1)	Adjusted Toxicity Value (ppb), as Total Recoverable, at Water Hardness[d]:			Adjusted Toxicity Value (ppb), as Dissolved[e], at Water Hardness:			SMAV
		m	h1	t1	x1	y1	15	50	286	15	50	286	
Fathead minnow, *Pimephales promelas*	S, M	1.72	75	8.7	4.3175	2.1633	0.546	4.3	87.0	0.464	3.68	73.9	
Fathead minnow, *Pimephales promelas*	F, M	1.72	40	5.6	3.6889	1.7228	1.04	8.2	165	0.881	6.99	140	
Fathead minnow, *Pimephales promelas*	F, M	1.72	36	7.4	3.5835	2.0015	1.64	13.0	261	1.40	11.1	222	
Fathead minnow, *Pimephales promelas*	S, M	1.72	38	9.4	3.6376	2.2407	1.90	15.1	303	1.61	12.8	257	
Fathead minnow, *Pimephales promelas*	S, M	1.72	39	9.7	3.6636	2.2721	1.87	14.9	299	1.59	12.6	254	
Fathead minnow, *Pimephales promelas*	S, M	1.72	44.8	14	3.8022	2.6391	2.13	16.9	340	1.81	14.4	289	
Fathead minnow, *Pimephales promelas*	F, U	0.341	33	3.9	3.4965	1.3610	2.98	4.5	8.1	2.5	3.8	6.9	
Fathead minnow, *Pimephales promelas*	F, U	0.341	274	4.8	5.6131	1.5686	1.782	2.7	4.9	1.5	2.3	4.1	
Fathead minnow, *Pimephales promelas*	F, M	1.72	44.7	9	3.8000	2.1972	1.38	10.9	219	1.17	9.28	186	
Fathead minnow, *Pimephales promelas*	F, M	1.72	38	16	3.6376	2.7726	3.23	25.7	515	2.75	21.8	438	
Fathead minnow, *Pimephales promelas*	F, M	1.72	46	10.7	3.8286	2.3702	1.56	12.3	248	1.32	10.5	211	
Fathead minnow, *Pimephales promelas*	F, M	1.72	48	10.98	3.8712	2.3961	1.48	11.8	236	1.26	10.0	201	
Fathead minnow, *Pimephales promelas*	F, M	1.72	255	150	5.5413	5.0106	1.15	9.1	183	0.975	7.74	155	
Fathead minnow, *Pimephales promelas*	F, M	1.72	54	11.1	3.9890	2.4069	1.23	9.7	195	1.042	8.26	166	
Fathead minnow, *Pimephales promelas*	F, M	1.72	46.1	5.3	3.8308	1.6677	0.768	6.1	122	0.653	5.18	104	
Fathead minnow, *Pimephales promelas*	F, M	1.72	75	6.3	4.3175	1.8405	0.395	3.1	63.0	0.336	2.67	53.5	
Fathead minnow, *Pimephales promelas*	F, M	1.72	48	11.75	3.8712	2.4639	1.59	12.6	253	1.351	10.7	215	
Fathead minnow, *Pimephales promelas*	F, M	1.72	255	110	5.5413	4.7005	0.841	6.7	134	0.715	5.67	114	
Fathead minnow, *Pimephales promelas*	F, M	1.72	46.1	3.9	3.8308	1.3610	0.565	4.5	90.0	0.481	3.8	76.5	
Fathead minnow, *Pimephales promelas*	F, M	1.72	75	5	4.3175	1.6094	0.314	2.5	50.0	0.267	2.1	42.5	
Fathead minnow, *Pimephales promelas*	F, M	1.72	44.4	6.7	3.7932	1.9021	1.04	8.2	165	0.881	6.99	140	
Speckled dace, *Rhinichthys osculus*	F, U	0.341	30	4.9	3.4012	1.5892	3.9	5.8	11	3.3	5.0	9	6.77
Speckled dace, *Rhinichthys osculus*	F, U	0.341	250	13.6	5.5215	2.6101	5.2	7.9	14.2	4.4	6.7	12.1	
Mottled sculpin, *Cattus bairdi*	F, U	0.341	30	5.3	3.4012	1.6677	4.2	6.3	11	3.6	5.4	10	7.04
Mottled sculpin, *Cattus bairdi*	F, U	0.341	250	13.6	5.5215	2.6101	5.2	7.9	14.2	4.4	6.7	12.1	

[a] Except for the final mean acute value in the first row, values are from Table 1 in USEPA 1987 adjusted to hardness of 50 mg/L as $CaCO_3$ using, except where noted, the pooled slope of 1.72 from USEPA 1980. Hard water in Goettl and Davies (1978) tests was unusually toxic and therefore not used in setting the pooled slope. For selection of the most sensitive result for the risk assessment, results from Goettl and Davies (1978) were adjusted using the pooled slope of 0.341 from the Goettl and Davies (1978) studies (0.098, 0.4815, 0.4444) were used for adjustments for these studies.

[b]Except where noted in table footnote (a), the acute slope is from Appendix B of current Recommended National Ambient WQC

[c]Natural log values of water hardness (x = Ln(hardness)) at 15, 76, 136, and 286 mg CaCO3/L are 2.7080, 3.9120, 4.3307, 4.9126, and 5.6560, respectively.

[c]Adjusted toxicity value (y) = m(x - x1) + y1 from point-slope linear relationship; see table footnote (c) for definition of x.

[d]Exp(y); see table footnote (b) for definition of y.

[e]The current Final Acute Value from Appendix B of current Recommended National Ambient WQC given as exp(1.72*[ln(hardness)], based on USEPA 1980. http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

[f] Values from Elnabarawy et al. 1986 were excluded from SMAV calculations. Results from the hard water used in this laboratory for this species and others in the USEPA 1987 appear to be more toxic than hard water at other laboratories for the same species, and values tend to be greater than a factor of 10 from other adjusted values. These studies are shaded in orange.

Table 38 Silver AWQC ACRs Adjusted to NOEC Basis

	Hardness (mg/L as CaCO3)	Acute value (ppb)	NOEC (ppb)	LOEC (ppb)	Chronic Value (ppb) = MATC(a)	ACR based on MATC	SMACR used to calculate FMACR for AWQC	ACR based on NOEC	SMACR Adjusted to NOEC	Reference
Cladoceran, *Daphnia magna*	73	11.2 [b]	10.5	21.2	14.92	0.7507		1.067		Nebeker 1982
Cladoceran, *Daphnia magna*	73	11.2 [b]	20.0	41.0	28.64	0.3911	0.5015	0.560	0.743	Nebeker 1982
Cladoceran, *Daphnia magna*	60	1.1	1.6	4.1	2.561	0.4295		0.688		Nebeker et al. 1983; Nebeker 1982
Rainbow trout, *Oncorhynchus mykiss*	36	9.2	0.36	0.51	0.4285	21.47	33.29	25.56	42.63	Nebeker et al. 1983
Rainbow trout, *Oncorhynchus mykiss*	28	6.4	0.09	0.17	0.124	51.61		71.11		Davies et al. 1978
Fathead minnow, *Pimephales promelas*	44.8	6.7	0.37	0.65	0.4904	13.66	13.66	18.11	18.11	Holcombe et al. 1983
Mysid, *Americamysis bahia*	30	249	11	32	18.76	13.2729		22.636		McKenny 1982; Lussier et al 1985
Mysid, Americamysis *bahia*	15-30	86	14	19	16.31	5.2728	8.51	6.143	12.68	McKenny 1982
Mysid, *Americamysis bahia*	15-30	132	9	25	15.00	8.8000		14.667		McKenny 1982
Final mean acute-to-chronic ration (FMACR)							15.70 [c]		21.39	

[a] Maximum acute threshold concentration (MATC) which is the geometric mean of the NOEC and LOEC values.
[b] Geometric mean of the two acute tests conducted at this laboratory, under same water hardness conditions (8.4 and 14.9 ppb).
[c] SMACR for the daphnids was not included in the FMACR calculations. ACRs should be greater than 1, and as explained in the USEPA (1980, and 1987) silver water quality criteria documents the presence of food in the chronic tests with the cladocerans appears to make the organisms less sensitive.

for the acutely sensitive mayfly. The 1987 FACR, adjusted for use of a NOEC, of 21.39 (Table 38) was used to estimate a chronic value for the fathead minnow.

Aquatic Plants

Summarized in Table 39 are the most sensitive aquatic plant endpoints used in previous assessment for silver. These values are based on silver data within OPP's files and selected open literature: EPA (1987) draft ambient aquatic life criteria document; Eisler (1996) synoptic review of silver hazards to fish, wildlife, and invertebrates; Howe and Dobson (2002) World Health Organization synoptic review of silver and silver compound fate and effects.

Table 39 Summary of Silver Toxicity to Aquatic Plants

Plant	Toxicity Value	Source
Freshwater green alga, *Selenastrum capricornutum*	4-day IC_{50} = 2.6 ppb (chlorophyll *a*)	USEPA 1987
Saltwater dinoflagellate, *Prorocentrum mariaelebouriae*	5-day IC_{50} = 3.3 ppb (7.5 ppt salinity, growth)	Eisler 1996; Howe and Dobson, 2002

Plant	Toxicity Value	Source
Saltwater diatom, *Skeletonema costatum*	5-day IC_{50} = 5.9 ppb (7.5 ppt salinity, growth)	Eisler, 1996; Howe and Dobson, 2002
Red alga, *Champia parvula*)	28-d NOAEC = 1.2 ppb (cystocarp formation)	EPA, 1987
Blue-green *Micryocystis aeruginosa* and *Cylindrosperum licheniforme*	IC_{50} = 420 ppb	EPA, 1980
Duckweed, *Lemna minor*	28-d IC_{50} = 270 ppb	EPA, 1987/ (Brown and Rattigan, 1979)
Terrestrial Plant – lettuce (germination), *Lactuca sativa*	>750 ppb	Howe and Dobson, 2002

Ecotoxicity Data for Zinc

Terrestrial Animals

There is one acute oral study (MRID 00155226) and one sub-acute dietary study (MRID 00155225) using Bobwhite quail, *Colinus virginianus*, on high purity grade zinc oxide contained in the in-house database (Table 40). Zinc oxide is classified as a slightly to practically non-toxic substance. The acute oral LD_{50} expressed in terms of the amount of zinc is 487 mg Zn/kg (606 mg zinc oxide/kg). The dietary study with zinc oxide showed no effects at the highest dietary concentration tested for a LC_{50} > 4,016 ppm zinc (LC_{50} > 5000 ppm zinc oxide).

Table 40 Summary of Zinc Toxicity to Birds

Species, Age or size	% Purity	Design Exposure Type	Endpoints as Zinc, total [as test substance]	Toxicity Category of Test Substance	Study Classification/ Source/ Comments
Bobwhite quail, *Colinus virginianus*, 23 weeks old	Zinc oxide 100% (80.3% Zn)	Acute oral	14-d LD_{50} = 487 mg Zn/kg [606 mg/kg] Slope = 3.6	Slightly toxic	Acceptable/ MRID 00155226, ACC260702/
Bobwhite quail, *Colinus virginianus*, 11 days old	Zinc oxide 99% (79.5% Zn)	Dietary	8-d LC_{50} >4016 ppm [>5000 ppm]	Practically non-toxic	Acceptable/ MRID 00155225, ACC260702/

Published studies show that coturnix quail fed a diet containing 1.5% zinc oxide had reproductive effects. Mallards fed a diet of 3000-12,000 ppm zinc showed decreased feed consumption and body weight and laying hens showed decreased egg production, shell strength and hatchability on a diet containing 20,000 ppm zinc.

Aquatic Animals

The national ambient water quality criteria for zinc was used as the primary source of toxicity data for zinc (USEPA 1987b, 1995); tests were conducted with zinc chloride, zinc sulfate and zinc nitrate. There were acceptable acute toxicity values for 44 species of freshwater animals and include twenty-two species of fish, one species of amphibian, four species of molluscs, eight species of crustaceans. The acute total recoverable zinc AWQC is hardness-dependent: CMC = $e^{0.8473(\ln \text{hardness}) + 0.884}$. When normalized to a water hardness of 50 mg/L as $CaCO_3$ using the pooled slope of 0.8473, the acute toxicity ranges from 50.70 ppb zinc for a cladoceran, *Ceriodaphnia reticulata,* to 88,960 ppb zinc for a damselfly (USEPA 1995). The most sensitive invertebrate species selected for the risk assessment is the cladoceran, *C. reticulata* (Table 13). The most sensitive fish species selected for the risk assessment is the striped bass, *Morone saxatilis*, with a normalized 96-hour LC_{50} of 33.0 ppb zinc. These acute values are as total recoverable zinc, and are converted to the dissolved form using the AWQC conversion factor of 0.978 for zinc freshwater acute studies (Appendix B of current national recommended AWQ[30]). Chronic toxicity data are available for nine freshwater species and include two species of invertebrates and six species of fish. There was insufficient data to calculate a chronic AWQC based on the eight-family approach so an ACR method was used. The chronic AWQC is hardness-dependent: $CCC = e^{0.8473(\ln \text{hardness}) + 0.884}$. The range in sensitivity of chronic toxicity ranges from 46.73 ppb zinc to >5,243 ppb. The ACR approach used in the AWQC development was applied to the most acutely sensitive fish and invertebrate, expect the ACR was adjusted for chronic values being expressed on a NOAEC basis versus the MATC used in the zinc criteria document (Table 41 and Table 18). These chronic values are as total recoverable zinc, and are converted to the dissolved form using the AWQC conversion factor of 0.986 for zinc freshwater chronic studies[30].

There were acceptable acute toxicity values available for 26 species of saltwater invertebrates and seven species of fish. The invertebrate species tested include five species of molluscs and Y species of crustaceans. Acute toxicity ranged from 191 ppb for larvae of the cabezon, *Scorpaenichthys marmoratus*, to 320,400 ppb for adults of the clam *Macoma balthica* (USEPA 1987b). The most acutely sensitive fish species was the cabezon, *S. marmoratus* (96-hour LC_{50} = 141 ppb zinc), the most sensitive mollusc was embryos of the quahog clam, *Mercenaria mercenaria* (IC_{50} = 195 ppb zinc), and the most sensitive non-mollusc species was a crustacean, the lobster *Homarus americanus* (175 ppb zinc). These species were used in assessing acute risks to saltwater species. These acute values are as total recoverable zinc, and are converted to the dissolved form using the AWQC conversion factor of 0.946 for zinc saltwater acute studies[30]. There was one acceptable saltwater animal chronic study with zinc and it was with the mysid, *Americamysis bahia*. There was insufficient data to calculate a chronic AWQC based on the eight-family approach so an ACR method was used. The ACR approach used in the AWQC development was applied to the most acutely sensitive fish and crustacean, expect the ACR was adjusted for chronic values being expressed on a NOAEC basis versus the MATC used in the zinc criteria document (Table 41 and Table 19). These chronic values are as total recoverable zinc, and are converted to the dissolved form using the AWQC conversion factor of 0.946 for zinc saltwater chronic studies[30].

Table 41 Zinc AWQC ACRs Adjusted to NOEC Basis

Test Species	Hardness (mg/L as $CaCO_3$)	Acute value (ppb)	NOEC (ppb)	LOEC (ppb)	Chronic Value (ppb) = MATC	ACR based on MATC	SMACR used to calculate FMACR for AWQC	ACR based on NOEC	SMACR Adjusted to NOEC	Reference
Cladoceran, *Daphnia magna*	52-54	334	97	190	135.8	2.459	7.2601	3.443	8.687	Chapman et al. Manuscript
Cladoceran, *Daphnia magna*	104-105	525	43	52	47.29	11.1		12.2		Chapman et al. Manuscript

[30] http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm

Test Species	Hardness (mg/L as $CaCO_3$)	Acute value (ppb)	NOEC (ppb)	LOEC (ppb)	Chronic Value (ppb) = MATC	ACR based on MATC	SMACR used to calculate FMACR for AWQC	ACR based on NOEC	SMACR Adjusted to NOEC	Reference
Cladoceran, *Daphnia magna*	196-211	655	42	52	46.73	14.02		15.6		Chapman et al. Manuscript
Sockeye salmon, *Oncorhynchus nerka*	32-37	1470	>242		>242	<6.074	--	<6.074	--	Chapman 1978a
Chinook salmon, *Oncorhynchus tshawytscha*	23-25	97-701	270	510	371.1	0.2614-1.889	0.7027	0.359-2.60	0.996	Chapman 1975
Rainbow trout, *Salvelinus gairdneri*	25-26	430	140	547	276.7	1.554	1.554	3.071	3.071	Sinley et al. 1974
Brook trout, *Salvelinus fontinalis*	45.9	1996	534	1368	854.7	2.335		3.738	3.738	Holcombe et al. 1979
Fathead minnow, *Pimephales promelas*	46	600	78	145	106.3	5.644		7.692	7.692	Benoit and Holcombe 1978
Flagfish, *Jordanella floridae*	44	1500	26	51	36.41	41.2		57.7	--	Spehar 1976a,b
Final Mean ACR (FMACR)	--						1.994	--	2.984	
Mysid, *Mysidopsis bahia*	30	499	120	231	166.5	2.997	2.997	4.158	4.158	

[a] Maximum acute threshold concentration (MATC) which is the geometric mean of the NOEC and LOEC values.

Aquatic Plants

Except for the toxicity data identified contained within the US national AWQC documents for zinc (USEPA 1987b), no data on toxicity of zinc to aquatic plants has been submitted to support zinc pesticide registrations. Within this criteria document, studies that have standard endpoints used by AD for risk assessments (e.g., 4-day to 5-day IC_{50} or EC_{50} and NOAEC values for microalgae, 7-day to 14-day IC_{50} or EC_{50} values for duckweed) are summarized in Table 42. The range in sensitivities of aquatic plants was greater than that of animals. The 7-day incipient growth inhibition for the freshwater green algae was 30 ppb zinc, whereas five other green algae species in the *Chlorella* genus and two diatom species in the genus *Navicula* had EC_{50} values exceeding 1,000 ppb. A saltwater diatom, *Schroederelia schroederi*, was also more sensitive than two other saltwater diatom species with EC_{50} values >200 ppb. Vascular macrophytes as represented by duckweed and Eurasian watermilfoil with EC_{50} values $\geq$10,000 ppb zinc. There is insufficient information to adjust values to take into account the impact from water hardness. A study conducted by the Academy of Natural Sciences (1960), tested the diatom, *Navicula seminulum*, at water hardness of 58 and 174 mg/L at three temperatures 22, 28, and 30 °C. At 22 °C, there was no reduction in toxicity at 174 mg/L hardness versus 58 mg/L. At 28 and 30 °C, there was a decrease in sensitivity by a factor of about 1.5 to 2.4. There is insufficient information to develop a relationship for hardness so the lowest values were used for the assessment. The impact on risk conclusions is discussed in the uncertainty section.

Table 42 Summary of Zinc Toxicity to Aquatic Plants

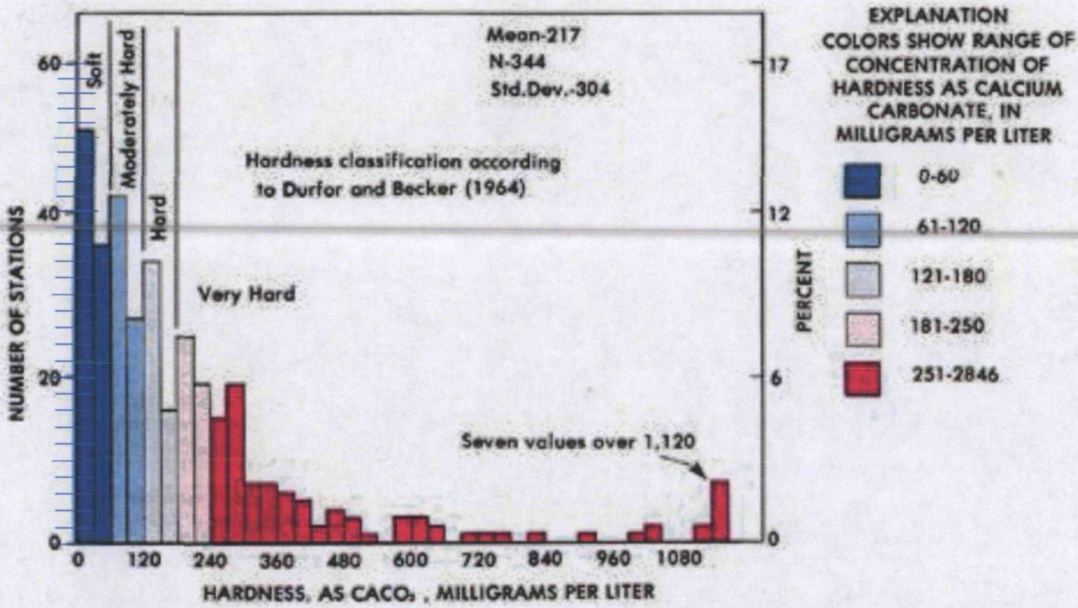
Plant	Toxicity Value as zinc, total	Source as cited in USEPA 1987
Freshwater species		
Green alga, Pseudokirchneriella subcapitata formerly called *Selenastrum capricornutum*	7-day IC_{50} = 30 ppb (incipient growth inhibition)	Bartlett et al. 1974
Green alga, Pseudokirchneriella subcapitata formerly called *Selenastrum capricornutum*	14-21-day IC_{50} = 50.9 ppb (biomass)	Turbak et al. 1986
Green alga, *Chlorella pyrenoidosa*	4-day LC_{50} = >200,000 ppb	Wong et al. 1979
Green alga, *Chlorella saccharophila*	4-day EC_{50} = 7,100 ppb	Rachlin et al. 1982
Green alga, *Chlorella salina*	4-day LC_{50} = >200,000 ppb	Wong et al. 1979
Green alga, *Chlorella vulgaris*	4-day EC_{50} = 2,400 ppb (growth)	Rachlin and Farran 1974
Green alga, *Scenedesmus quadricauda*	4-day LC_{50} = >200,000 ppb	Wong et al. 1979
Diatom, *Navicula incerta*	4-day EC_{50} = 10,000 ppb	Rachlin et al. 1982
Diatom, *Navicula seminulum*	5-day EC_{50} = 4,290 ppb 22 °C, 58 mg/L hardness	Academy of Natural Sciences 1960
	5-day EC_{50} = 1,590 ppb 28 °C, 58 mg/L hardness	
	5-day EC_{50} = 1,320 ppb 30 °C, 58 mg/L hardness	
	5-day EC_{50} = 4,050 ppb 22 °C, 174 mg/L hardness	
	5-day EC_{50} = 2,310 ppb 28 °C, 174 mg/L hardness	
	5-day EC_{50} = 3,220 ppb 30 °C, 174 mg/L hardness	
Diatom, *Navicula linearis*	5-day LC_{50} = 4,300 ppb, 294.6 mg/L hardness	Patrick et al. 1968
Duckweed, *Lemna minor*	4-day EC_{50} = 10,000 ppb (growth)	Wang 1986
Duckweed, *Lemna minor*	28-day EC_{50} = 67,700 ppb (tissue damage and death)	Brown and Rattigan 1979
Duckweed, *Lemna minor*	70-day NOEC $\geq$ 654 ppb (biomass)	Van der Werff and Pruyt 1982
Water starwort, *Callitriche plataycarpa*	73-day NOEC $\geq$ 654 ppb (biomass)	Van der Werff and Pruyt 1982
Eurasian watermillfoil, *Myriophyllum spicatum*	32-day EC_{50} = 21,600 ppb (root weight)	Stanley 1974
Nuttall's waterweed, *Elodea nuttallii*	73-day NOEC $\geq$ 654 ppb (biomass)	Van der Werff and Pruyt 1982
Saltwater species		
Diatom, *Navicula incerta*	4-day EC_{50} = 10,100 ppb (growth)	Rachlin et al. 1982
Diatom, *Natzschia closterium*	4-day EC_{50} = 271 ppb (growth)	Rosko and Rachlin 1975
Diatom, *Schroederelia schroederi*	4-day EC_{50} = 19.01 ppb, 32 ppt salinity (growth)	Kayser 1977, calculated from author's data
Dinoflageliate, *Gymnodinium splendens*	4-day EC_{50} = 3,716 ppb, 32 ppt salinity (growth)	Kayser 1977, calculated from author's data
Dinoflageliate, *Procentrum micans*	4-day EC_{50} = 319 ppb, 32 ppt salinity (growth)	Kayser 1977, calculated from author's data
Coccolithophorid, Cricosphaera carterae	4-day EC_{50} = 76.7 ppb (growth)	Stillwell 1977
Giant kelp (young fronds), Macrocystis pyrifera	4-day EC_{50} = 10,000 ppb (photosynthetic rate)	Clendenning and North 1959

Appendix D Determination of Representative Softwater and Hardwater Conditions for National Assessment of Inland Freshwater Marinas

The evaluation of risks from leaching of active ingredients and/or their transformation products or degradates from antifoulant paint to a freshwater marina is relatively new for the antimicrobials division. The agency has conducted such modeling recently but the need to account for water chemistries that affect toxicity such as in the case of metals has not been conducted previously in this setting. Freshwater ambient water quality criteria for silver and zinc are hardness-dependent, and for the purposes of this assessment the hardness-dependent relationship for copper developed in 1995 rather than the more recent 2007 biotic ligand model approach was used to estimate risk.

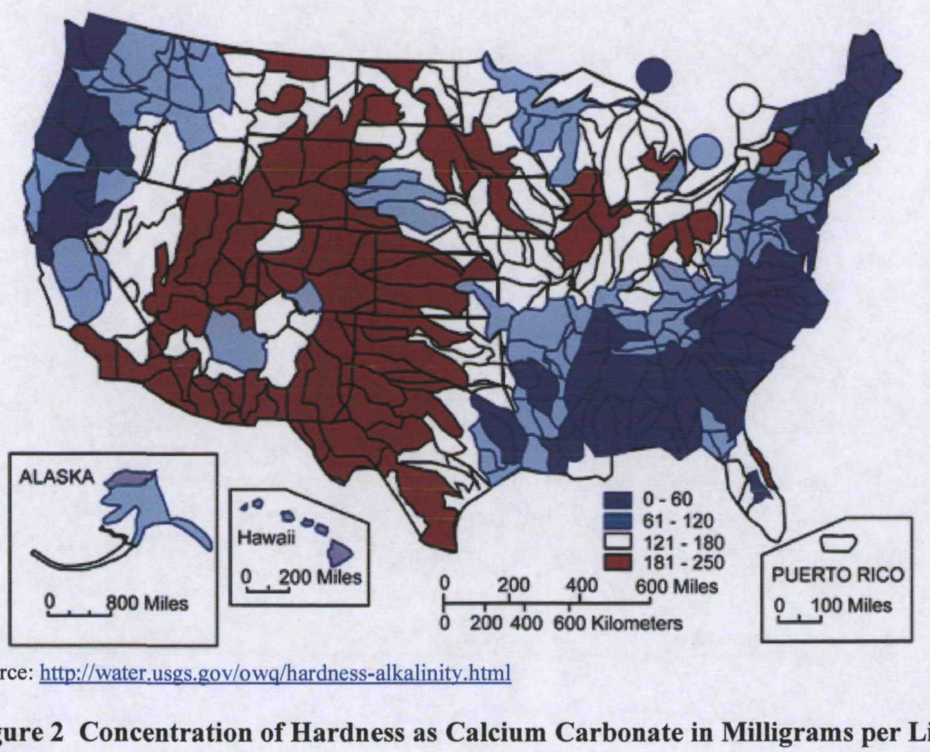
To use a hardness-dependent effects approach, the hardness condition for use in the model needed to be determined. There are a number of potential options for selection of such a value. Currently there is a data gathering and analysis effort underway by interested parties to better parameterize the freshwater inland marina scenarios for U.S. conditions. However, this effort is not complete at this time and given the timeframe and resources, an existing, readily available analysis on the pattern and distribution of water hardness in U.S. waters by the United States Geological Survey (USGS) [31] was used to develop interim values. A frequency chart of mean values of hardness at 344 stations across the continental U.S., Hawaii, Alaska, and Puerto Rico during the 1975 water year is presented on the website (included here-in as Figure 1) along with isopleth maps of water hardness in the continental U.S., Hawaii, Alaska and Puerto Rico (included here-in as Figure 2); these were originally taken from Briggs and Ficke (1977). Although the data is from 1975, the USGS on the site states that water hardness conditions in the U.S. have been found to be are relatively stable over time and that the data presented on this site "…has been found to be accurate and useful in current assessments." The frequency information in Figure 1 was tabulated in Table 43 to obtain quick approximations of the median soft water and median very hard water concentrations, to bound water hardness estimates. Of the 344 stations, 25% represented soft water conditions (0 to 60 mg/L as $CaCO_3$), which from the isopleth maps are conditions representative of surface waters in Hawaii, the Atlantic coastal states except Florida, and large portions of the north eastern and south eastern U.S., and large portions of the Pacific northwest. About a third of the stations (34.5%) had moderately hard (61 to 120 mg/L as $CaCO_3$) to hard (121 to 180 mg/L as $CaCO_3$) water conditions and the remaining approximately 40% had very hard (>180 mg/L as $CaCO_3$) water. In the soft water category the median station (44) would fall within the 0 to 30 mg/L as $CaCO_3$ bin, the midpoint of this bin (15 mg/L as $CaCO_3$) was selected for the interim soft water inland marina scenario. In the very hard water category the median station (69) would fall within the 271 to 300 mg/L as $CaCO_3$ bin, the midpoint of this bin (286 mg/L as $CaCO_3$) was selected for the interim hard water inland marina scenario.

[31] http://water.usgs.gov/owq/hardness-alkalinity.html



Source: http://water.usgs.gov/owq/hardness-alkalinity.html

Figure 1 Frequency Chart of Mean Water Hardness at 344 Water Stations in 1975 in the U.S. and Puerto Rico



Source: http://water.usgs.gov/owq/hardness-alkalinity.html

Figure 2 Concentration of Hardness as Calcium Carbonate in Milligrams per Liter

Table 43 Estimate of Representative Soft and Hard Water Conditions for Freshwater Inland Marina Scenarios

Classification	No. of NASQN Stations	Hardness as mg $CaCO_3$/L			Percent of NASQN Stations	Midpoint Estimation	
		Range	Midpoint	Weighted Average		Median Station No.	Class Midpoint
Soft Water	51	0-30	15	28	25.3	43.5	15
	36	31-60	45.5				
Moderately Hard	42	61-90	75.5	87	20.0	34.5[a, b]	76[a, b]
	27	91-120	105.5				
Hard	34	121-150	135.5	145	14.5	25[a, b]	136[a, b]
	16	151-180	165.5				
Very Hard	25	181-210	195.5	353	7.3	69	286
	19	211-240	225.5		5.5		
	15	241-270	255.5		4.4		
	19	271-300	285.5		5.5		
	7	301-330	315.5		2.0		
	7	331-360	345.5		2.0		
	6	361-390	375.5		1.7		
	5	391-420	405.5		1.5		
	2	421-450	435.5		0.6		
	4	451-480	465.5		1.2		
	3	481-510	495.5		0.9		
	1	511-540	525.5		0.3		
	0	541-570	555.5		0.0		
	3	571-600	585.5		0.9		
	3	601-630	615.5		0.9		
	2	631-660	645.5		0.6		
	0	661-690	675.5		0.0		
	1	691-720	705.5		0.3		
	1	721-750	735.5		0.3		
	1	751-780	765.5		0.3		
	0	781-810	795.5		0.0		
	1	811-840	825.5		0.3		
	0	841-870	855.5		0.0		
	0	871-900	885.5		0.0		
	1	901-930	915.5		0.3		
	0	931-960	945.5		0.0		
	0	961-990	975.5		0.0		
	1	991-1020	1005.5		0.3		
	2	1021-1050	1035.5		0.6		
	0	1051-1080	1065.5		0.0		
	0	1081-1110	1095.5		0.0		
	2	1111-1120	1115.5		0.6		
	7	>1120			2.0		
Total	344						

[a] The midpoint of moderately hard to hard stations combined is the 60th station in this group which falls within the 91-120 mg/L as $CaCO_3$ bin. The midpoint of this bin is 106 mg/L as $CaCO_3$.

[b] The median station would be number 172, this station falls within the 121-150 mg/L as $CaCO_3$ bin, and the midpoint of this bin is 136 mg/L as $CaCO_3$.

Appendix E. Steady-State Leach Rate RQs

The leaching rates from the copper and zinc declined rapidly in the study to a relatively-steady state by 21-24 days (MRID 48772001). For copper, the leaching rates declined from a maximum of 71.6 μg/cm^2/day at Day 1 to a steady-state value of 0.77-3.1 μg/cm^2/day from 24-91 days (end of study). The average copper leaching rate from 24-91 days was 1.4 μg/cm^2/day, or 51 times less than the maximum. For zinc, leaching rates declined from a maximum of 1.86 μg/cm^2/day at Day 1 to a steady-state value of 0.2-0.98 μg/cm^2/day by 21-91 days. The average zinc leaching rate from 21-91 days was 0.31 μg/cm^2/day, or six times lower than the maximum rate.

Unlike copper and zinc, silver leaching rates were relatively constant at 1.0 μg/cm^2/day throughout most of the study duration and reached a maximum value of 1.5 μg/cm^2/day at Day 21. The average silver leaching rate throughout the study duration was 1.06 μg/cm^2/day or about 71% of the maximum rate.

RQs were calculated using EECs based on maximum leaching rate. This is the rate that would be expected for newly applied paint. Not all boats will have fresh antifoulant paint on their hulls or bottoms at the same time. Using the steady-state conditions identified in previous paragraphs, an estimate of the impact to EECs was made by first taking the ratio of the maximum observed leaching rate divided by the steady-state rate and dividing the EECs based on the maximum leach rate to obtain steady-state maximum and average EECs. The maximum:steady-state leaching rate ratios were 23.1, 1.9, and 1.42 for Cu, Zn, and Ag, respectively. This approach was validated by comparing the results to an actual model run using the steady-state leaching rate for each metal in the freshwater large marina scenario. For copper, zinc, and silver, the estimated concentrations using the steady-state leaching rates were 15.6-17.2X, 1.3-1.4X, and 1.1-1.2X lower than those of the maximum leaching rates, respectively.

As a result, the estimated, the dissolved concentrations using the other scenarios and the maximum leaching rate for each metal were divided by the minimum ratio of EECs using the steady-state leaching rates for each metal. The adjustment factors were 15.6, 1.3, and 1.1 for copper, zinc, and silver, respectively. A summary of steady-state EECs are provided in **Error! Reference source not found.**.

Table 44 Dissolved Concentrations in Water (μg/l) in Modeled Water Bodies using Steady-State Leaching Rates for Cu, Zn, and Ag.

Metal	Freshwater Marina				Saltwater			
	Small (75 boats)		Large (299 boats		Commercial harbor		Default saltwater marina	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Copper	3.9	2.4	11.7	7.2	2.1	0.74	7.2	5.0
Zinc	1.2	0.77	3.8	2.3	0.67	0.24	2.3	1.7
Silver	1.2	0.73	3.8	2.4	0.63	0.14	2.3	1.6

For silver there is not much of an impact on RQs because the maximum and steady-state leach rates do not differ significantly. For zinc, because there were no exceedances of LOCs for the saltwater marina and commercial harbor or freshwater, hardwater conditions the steady-state has little impact except reducing exceedance for listed species. Exceedances for copper are still expected, an example for the saltwater marina and commercial harbor are provided in **Error! Reference source not found.**.

Table 45 Aquatic organism RQs for saltwater marina and commercial harbor scenarios from leached copper – Steady-State Leach Rate

Receptor Group	Risk Scenario	Copper (ppb) dissolved			RQs	
		Toxicity Endpoints	EECs			
			Marina	Commercial Harbor	Marina	Commercial Harbor
Saltwater fish	Acute	9.88	7.2	2.1	*0.7*	*0.2*
	Chronic	3.2	5	0.74	**1.6**	<1
Saltwater crustacean	Acute	14.1	7.2	2.1	**<u>0.51</u>**	*0.15*
	Chronic	4.6	5	0.74	**1.1**	<1
Saltwater mollusk	Acute	4.6	7.2	2.1	**<u>1.6</u>**	*0.46*
CMC	FAV/2	4.0	7.2	2.1	**1.8**	<1
CCC	Chronic	2.6	5	0.74	**1.9**	<1
Aquatic Plants, Nonvascular	Nonlisted	1.2	7.2	2.1	**<u>6.0</u>**	**<u>1.8</u>**
	Listed	0.8	7.2	2.1	*9.0*	*2.6*
Aquatic Plants, Vascular	Nonlisted	119	7.2	2.1	<1	<1
	Listed	5.2	7.2	2.1	*1.4*	<1

Appendix F. Biotic Ligand Model Considerations

Risk estimates for evaluating potential adverse effects to freshwater aquatic animals were calculated using endpoints adjusted for water hardness alone. While this method accounts for some effects of water chemistry on toxicity of copper to aquatic animals, it can result in an overestimate of sensitivity and an over estimate of risk under some environmental conditions. The OW published copper criteria based on the BLM (USEPA 2007b) method in 2007, but the method requires parameterization of several water chemistry exposure conditions for application of the method. The freshwater inland marina scenarios currently being used by the agency do not have these values parameterized for a national assessment in the U.S. Therefore, RQs could not be calculated at this time using BLM adjusted effect endpoints. The degree to which this may have impacted risk estimates were obtained using Figure 5 from the USEPA (2007b) copper criteria document (included here-in as Figure 3**Error! Reference source not found.**). There is a very discernable interaction in the size of effect at different DOC levels. The hardness-dependent method gives CMC values lower than the BLM at a DOC of 2 mg/L up to about a water hardness of 150 mg/L but appears to provide higher values around 275 mg/L $CaCO_3$. A comparison of the hardness-dependent and BLM CMCs at 20, 110, and 285 mg/L hardness and 2, 5, and 10 mg/L DOC for the BLM are provided in Table 47**Error! Reference source not found.** based on estimates from Figure 3**Error! Reference source not found.**. The hardness levels are representative of the soft and hard water exposure scenarios used to estimate RQs in this assessment, and the median hardness of the 344 stations used to estimate interim water hardness values for this assessment (see Appendix D).

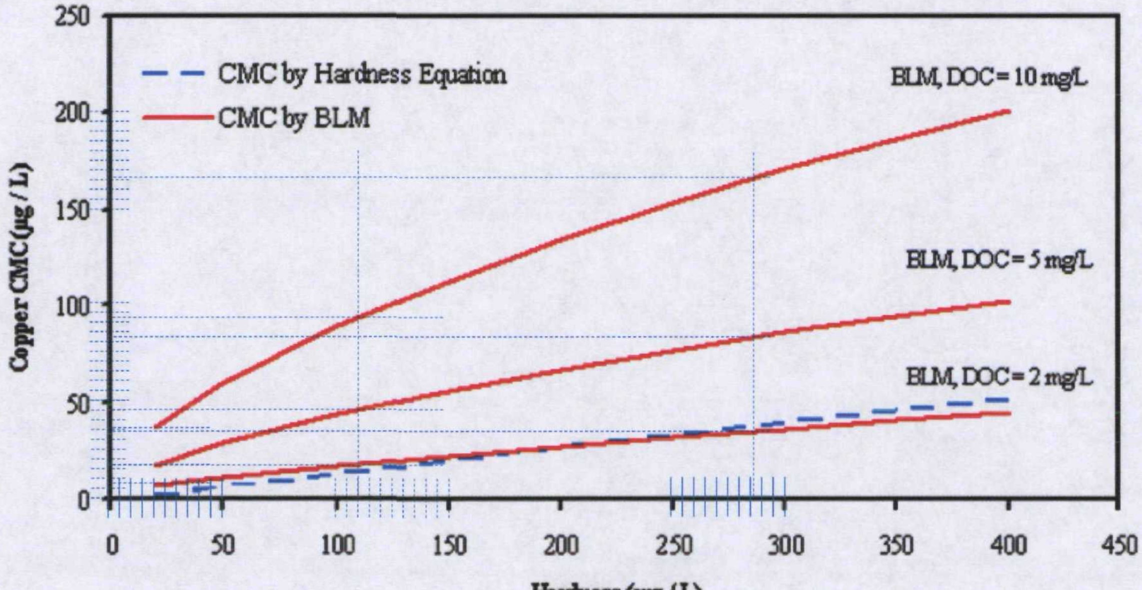


Figure 3 Figure 5 from USEPA (2007b). Comparison of CMC calculated by BLM or Hardness Equation Alkalinity (11-245 mg $CaCO_3$/L) and pH (7.3-8.7) Co-vary with Hardness

Table 46 Calculated Hardness-Dependent and Approximated CMCs (in ppb) from Figure 3Error! Reference source not found. at Water Hardness of 20, 110, and 285 mg/L as $CaCO_3$

Hardness (as mg/L $CaCO_3$)	Hardness-Dependent CMC	BLM, DOC = 2 mg/L CMC	BLM, DOC = 5 mg/L CMC	BLM, DOC = 10 mg/L CMC
20	2.6	7.	16	35
110	13.0	17	45	82
285	31.0	35	93	165

Table 47 RQs based on Approximated BLM CMCs at DOC of 2, 5, and 10 mg/L and water hardness of 20, 110, and 285 mg/L as $CaCO_3$ – Maximum Leach Rate

Hardness (as mg/L $CaCO_3$)	Small Inland Freshwater Marina			Large Inland Freshwater Marina		
	BLM, CMC at DOC			BLM, CMC at DOC		
	2	5	10	2	5	10
20	**8.6**[(a)]	**3.8**	**1.7**	**26**	**11**	**5.2**
110	**3.5**	**1.3**	<1	**11**	**4.0**	**2.2**
285	**1.7**	<1	<1	**5.2**	**2.0**	**1.1**

[(a)] Values in bold exceed the CMC (i.e., RQ>1).

For this assessment the representative or typical concentrations of DOC in inland fresh water marinas has not been evaluated at this time. For natural surface waters Wetzel (2001) reports the total organic carbon (TOC) content to generally be in the range of 1 – 30 mg carbon/L, with higher values being usually found either in productive habitats (e.g., shallow waters of wetlands) or in organically polluted waters. DOC usually composes a large portion of the TOC in natural waters. Wetzel (2001) reports that the median DOC content of the water of natural aquatic ecosystems is on the order of 30.3 mg carbon/L for bog water, 15.3 mg carbon/L for wetlands-marshes, 10.3 mg carbon/L for eutrophic lakes, 5.0 mg carbon/L for rivers, and 2.0 mg carbon/L for oligotrophic lakes. In softwater conditions using the maximum leach rate, while use of the BLM method would have resulted in lower RQs for copper, the CMC is still exceeded across the DOC range of 2 to 10 mg carbon/L as it is for the median water hardness of 110 mg/L as $CaCO_3$, except for the small inland marina under very hard water conditions. While in small inland marina, exceedance of the CMC would not be expected at DOC $\geq$5 mg carbon/L, in softwater conditions and in large marinas exceedances are still indicated. The steady-state condition would reduce these but still result in exceedances.